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## Effects of dopants on the isothermal decomposition kinetics of potassium metaperiodate

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**Abstract:** The isothermal decomposition and kinetics of potassium metaperiodate ( $\text{KIO}_4$ ) were studied by thermogravimetry as a function of the concentration of dopants. The thermal decomposition of  $\text{KIO}_4$  proceeds mainly through two stages: an acceleration period up to  $\alpha = 0.50$  and a decay stage. The thermal decomposition data for both doped and untreated  $\text{KIO}_4$  were found to be best described by the Prout–Tompkins Equation. The  $\alpha$ - $t$  data of doped and untreated samples of  $\text{KIO}_4$  were subjected to isoconversional studies for the determination of the activation energy values. The isoconversional studies of the isothermal decomposition of untreated and doped samples of  $\text{KIO}_4$  indicated that the thermal decomposition of  $\text{KIO}_4$  proceeds through a single kinetic model, the Prout–Tompkins model, throughout the entire range of conversion, as opposed to earlier observations.

**Keywords:** doping; isoconversional analysis; isothermal decomposition;  $\text{KIO}_4$ .

### INTRODUCTION

Thermal decomposition studies are one of the most common and widely used techniques employed to obtain insight into the elementary steps of solid-state reactions. The reactivity of solids is greatly modified by pre-treatment, such as doping, pre-compression, pre-heating, *etc.* The nature of influence of the pre-treatment provides valuable information of the elementary steps of solid-state reactions and thereby on the mechanism and control of solid-state reactions.<sup>1,2</sup> Kinetic studies are one of the important applications of thermal analysis. Solid-state kinetic data are of practical interest for a large and growing number of technologically important processes. A large number of reviews are available in the literature on such processes.<sup>3–10</sup>

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The methods of kinetic analysis can be classified based on the experimental conditions selected and the mathematical analysis performed. Experimentally, either isothermal or non-isothermal methods can be used. The isothermal methods are based on the initial assumption that a single conversion function and a single set of Arrhenius parameters,  $A$  and  $E$ , apply over the full range of the degrees of conversion. The main problem in isothermal kinetic analysis is that a sample requires some time to reach the experimental temperature. We solved this problem by fabricating a thermobalance particularly for studying the isothermal kinetics of solid-state reactions. The effects of pre-treatments on the thermal reactivity of several high-energy solids, such as halates and perchlorates, were reported<sup>11–19</sup> that throw light on the mechanism of their decomposition. Thermal decompositions of halates and perchlorates, which occupy an important place in modern solid-state chemistry, are extremely sensitive to the presence of impurities, additives, *etc.*, and more data of this kind are desirable.

According to thermoanalytical studies,  $\text{KIO}_4$  decomposes in two steps.<sup>20,21</sup> At about 570 K,  $\text{KIO}_4$  decomposes with heat evolution to potassium iodate ( $\text{KIO}_3$ ) and oxygen. The decomposition of  $\text{KIO}_3$  to  $\text{KI}$  occurs in the range 780–800 K. In the thermal decomposition of  $\text{KIO}_4$ , the identification of the six-valent iodine compound,  $\text{K}_2\text{IO}_4$ , analogous to the compounds,  $\text{M}_2\text{IO}_4$  formed in the decomposition of lithium and sodium periodates has not been realised. The effects of several pre-treatments on the kinetics and mechanism of the thermal decomposition of  $\text{KIO}_4$  have been studied. It was observed that  $\text{KIO}_4$  decomposes *via* the Prout–Tompkins mechanism. Earlier investigations<sup>13,16,18,19</sup> showed that the isothermal decomposition of  $\text{KIO}_4$  follows Prout–Tompkins kinetics at all temperatures studied and it was proposed that the probable rate determining step in the thermal decomposition of  $\text{KIO}_4$  is the transfer of an electron from the periodate anion to the potassium cation, rather than the rupture of the I–O bond or the diffusion of cations/anions.

Studies on the effect of metal oxide ( $\text{CuO}$ ,  $\text{MnO}_2$  and  $\text{TiO}_2$ ) additives on the thermal decomposition kinetics of potassium metaperiodate ( $\text{KIO}_4$ ) to potassium iodate ( $\text{KIO}_3$ ), in air by thermogravimetry under isothermal conditions,<sup>18</sup> revealed that irrespective of whether p- or n-type, the metal oxides had little or no influence on the rate of the decomposition, except for a small decrease when the oxide concentration was as high as 10 wt. %. The rate law for the decomposition of  $\text{KIO}_4$  (Prout–Tompkins model) remained unaffected by the additives. The behaviour of mechanical mixtures of  $\text{KIO}_4$  with n- and p-type semi-conducting oxides suggests that the electron work functions of these oxides might be smaller than that of  $\text{KIO}_4$ ; hence, they lack electron acceptor property with respect to  $\text{KIO}_4$  and thus fail to favour electron transfer processes.

In continuation of investigations on the thermal behaviour of periodates of alkali metals,<sup>13,16–19</sup> in this paper, the results of isoconversional analysis of the

isothermal decomposition kinetics of doped and untreated samples of  $\text{KIO}_4$  in the temperature range 560–580 K are reported. Isoconversional kinetics rests upon the evaluation of the dependence of the effective activation energy on conversion and using this dependence for making kinetic predictions and for exploring the mechanism of thermal processes.

#### EXPERIMENTAL

All the employed chemicals were of AnalaR grade reagents from Merck. Doped samples of  $\text{KIO}_4$ , at four concentrations, viz.,  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$  and 0.1 mol % were prepared by the method described earlier.<sup>13,16</sup>  $\text{BaCl}_2$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{SO}_4$  and  $\text{K}_3\text{PO}_4$  were used for doping  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , respectively. The thermogravimetric (TG) measurements in static air were performed on a custom fabricated thermobalance,<sup>16</sup> an upgraded version of Hooley.<sup>22</sup>

A major problem<sup>23</sup> in isothermal experiments is that the 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. Hence a thermobalance was fabricated particularly for isothermal studies, in which loading of the sample is possible at any time after attaining the desired temperature. The operational characteristics of the thermobalance are: accuracy; balance:  $\pm 1.0 \times 10^{-5}$  g, temperature:  $\pm 0.5$  K, sample mass:  $5 \times 10^{-2}$  g, particle size: 90–106  $\mu\text{m}$  and crucible: platinum. The fraction of solid decomposed ( $\alpha$ ) was measured as a function of time ( $t$ ) at five different temperatures, viz., 560, 565, 570, 575 and 580 K.

The  $\alpha$ - $t$  data, in the  $\alpha$  range 0.05–0.95, of doped and untreated samples of  $\text{KIO}_4$  were subjected to isoconversional studies for the determination of the apparent activation energy as a function of  $\alpha$  from the sets of isothermals obtained. The activation energy value (for a given value of  $\alpha$ ) of the decomposition reaction was calculated from a plot of  $\ln t$  ( $t$  being the time required to reach a given value of  $\alpha$  at a constant temperature  $T$ ) versus the corresponding reciprocal of the temperature ( $1/T$ ).

#### RESULTS AND DISCUSSION

The  $\alpha$ - $t$  curves for the decomposition of the pure and doped samples of  $\text{KIO}_4$  at 560 K are shown in Fig. 1. Similar curves were obtained for all other samples of  $\text{KIO}_4$  (doped and untreated) at all temperatures. The decomposition proceeded mainly through two stages: *i*) an acceleration period up to  $\alpha = 0.50$  and *ii*) a decay stage.

The  $\alpha$ - $t$  data in the  $\alpha$  range 0.05–0.95 were fitted to various solid state kinetic equations, given in Table S-I of the Supplementary material, using the method of weighted least squares, as described earlier.<sup>13</sup> The Prout–Tompkins Equation,<sup>24</sup>  $\ln(\alpha/(1-\alpha)) = kt$ , which is the simplest case of an autocatalytic reaction, gave the best fits for all the studied temperatures. A typical fit for the Prout–Tomkin model for the decomposition of the untreated sample of  $\text{KIO}_4$  at 560 K is shown in Fig. 2. Typical fits for all kinetic models described in Table S-I for the decomposition of the untreated sample of  $\text{KIO}_4$  at 560 K are shown in Figs. S-1–S-4 of the Supplementary material. Similar fits were obtained for all

other samples of  $\text{KIO}_4$  and at all temperatures (not shown). Separate kinetic analyses of the  $\alpha$ - $t$  data corresponding to the acceleration region ( $\alpha$  range 0.05–0.5) and the decay region ( $\alpha$  range 0.5–0.95) showed that the acceleration stage was best fitted by the Prout–Tompkins equation itself, whereas the decay stage was better fitted by the contracting area equation.<sup>13,16,19</sup> Doping did not change the basic shape (sigmoid) of the  $\alpha$ - $t$  plots and the decomposition proceeded through the two stages mentioned in the case of pure  $\text{KIO}_4$ , obeying the same rate laws mentioned above for the two decomposition ranges.

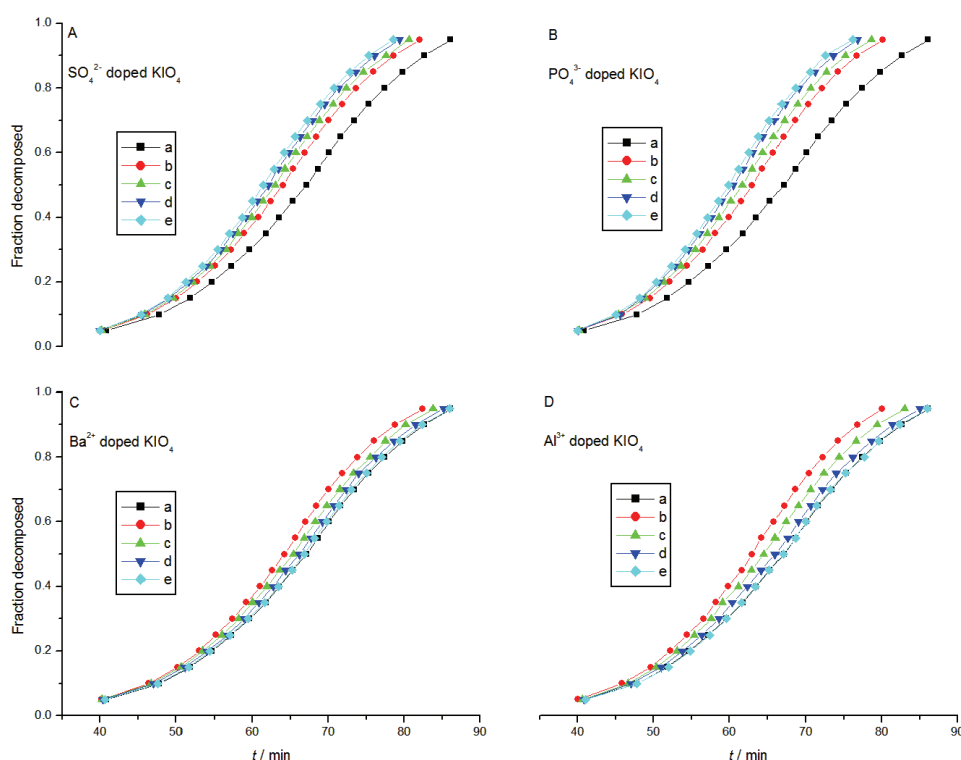


Fig. 1. The  $\alpha$ - $t$  curves for the isothermal decomposition of A: sulphate; B: phosphate; C: barium- and D: aluminium-doped  $\text{KIO}_4$  at 560 K; 0 mol %, a,  $10^{-4}$  mol %, b,  $10^{-3}$  mol %, c,  $10^{-2}$  mol %, d, 0.1 mol %, e; in C and D, curve a is superimposed on curve e.

The  $\alpha$ - $t$  data, in the  $\alpha$  range 0.05–0.95 with an interval of 0.05, of the untreated and doped samples of  $\text{KIO}_4$  were also subjected to isoconversional studies for the determination of the apparent activation energy as a function of  $\alpha$ . A plot of  $\ln t$  ( $t$  being the time required to reach a given value of  $\alpha$  at a constant temperature  $T$ ) versus the corresponding reciprocal of the temperature ( $1/T$ ) leads to the activation energy for the given value of  $\alpha$ . Typical isoconversional plots for the isothermal decomposition of sulphate doped  $\text{KIO}_4$  (at different conver-

sions) are shown in Fig. 3. Similar plots were obtained for all other doped samples of  $\text{KIO}_4$ . Values of slope and correlation coefficient obtained for the isoconversional plots of sulphate and barium doped samples of  $\text{KIO}_4$  at different dopant concentrations at different conversions are given in Tables I and II, respectively. Similar values were obtained for isoconversional plots of all other doped samples of  $\text{KIO}_4$ . In all cases, the isoconversional plots gave good correlations. A plot of the apparent activation energy *vs.* conversion for untreated  $\text{KIO}_4$  is shown in Fig. 4 and those of the doped samples in Fig. 5.

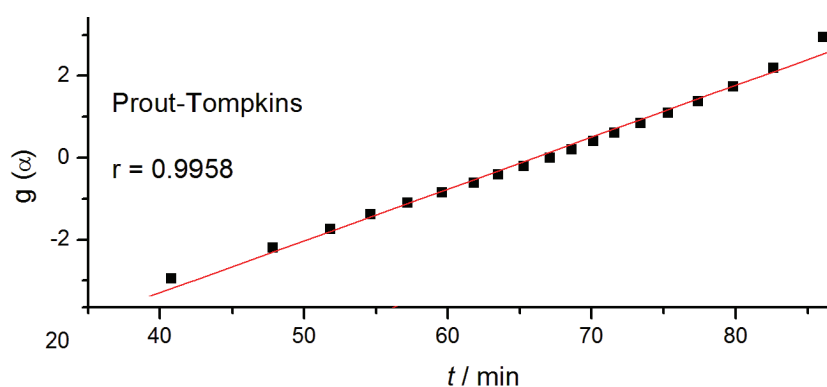


Fig. 2. Typical model fitting least square plot for the Prout–Tompkins model for the decomposition of  $\text{KIO}_4$  at 560 K.

Philips and Taylor<sup>25</sup> proposed that the rupture of the I–O bond determines the rate of the decomposition of  $\text{KIO}_4$  to  $\text{KIO}_3$ . Contrary to the observation of Hill,<sup>26</sup> they pointed out that the autocatalytic stage does not involve a diffusion chain and reported an activation energy ( $E$ ) value of  $191 \text{ kJ mol}^{-1}$  for the decomposition of  $\text{KIO}_4$ . Our earlier investigations<sup>13,16,18,19</sup> showed that the isothermal decomposition of  $\text{KIO}_4$  follows Prout–Tompkins kinetics at all temperatures studied with an  $E$  value of  $206 \pm 3 \text{ kJ mol}^{-1}$ . The acceleration stage was best described by the Prout–Tompkins equation itself, with an  $E$  value of  $218 \pm 3 \text{ kJ mol}^{-1}$ . However, the decay stage was best represented by the contracting area equation with an  $E$  value of  $185 \pm 3 \text{ kJ mol}^{-1}$ . Based on these previous results, we suggested that  $\text{KIO}_4$  decomposes in accordance to the Prout–Tompkins model with two dimensional nucleus growth up to 50 % decomposition, and thereafter through the contracting area law. Several authors<sup>17,25,27–30</sup> reported such a description of the reaction kinetics using different rate laws for different ranges of  $\alpha$ . We reported earlier that the rate law and the activation energy of the decomposition remained unaltered by doping and observed that the basic mechanism of the decomposition was not affected by doping, the only effect being a modification in the concentration of active sites.

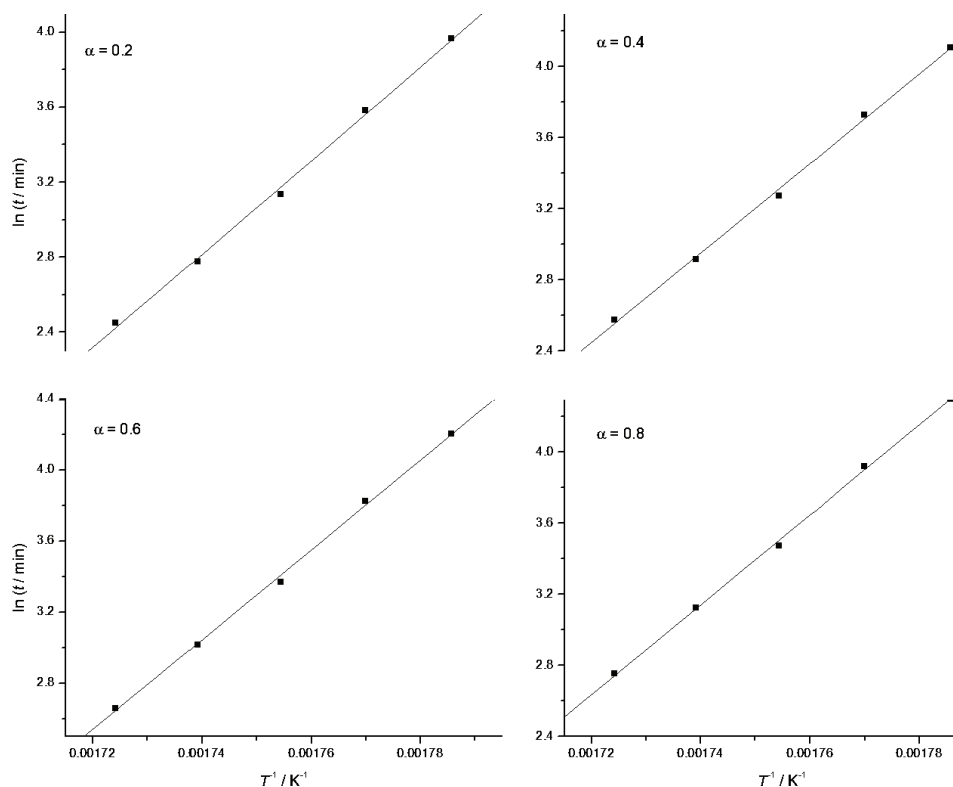


Fig. 3. Typical isoconversional plots for sulphate doped  $\text{KIO}_4$  at 560 K.

TABLE I. Values of slope and correlation coefficient obtained for the isoconversional analysis of sulphate-doped samples of  $\text{KIO}_4$  at different dopant content and at different conversions

$\alpha$	Dopant content, mol %							
	$10^{-4}$		$10^{-3}$		$10^{-2}$		0.1	
	Slope, $\text{K}^{-1}$	$r$	Slope, $\text{K}^{-1}$	$r$	Slope, $\text{K}^{-1}$	$r$	Slope, $\text{K}^{-1}$	$r$
0.05	24351.5	0.9982	24492.5	0.9996	24598.1	0.9987	24596.9	0.9985
0.10	24609.0	0.9985	24822.4	0.9996	24914.3	0.9988	24908.9	0.9988
0.15	24835.5	0.9987	24973.9	0.9988	25066.0	0.9990	25123.3	0.9989
0.20	24923.0	0.9989	25008.7	0.9988	24764.7	0.9981	25203.3	0.9989
0.25	24954.1	0.9988	25146.2	0.9989	25351.4	0.9991	25314.1	0.9989
0.30	25025.9	0.9989	25231.0	0.9990	25365.8	0.9991	25352.1	0.9989
0.35	25126.7	0.9990	25269.2	0.9991	25405.5	0.9992	25352.0	0.9990
0.40	25182.6	0.9991	25372.0	0.9992	25464.2	0.9992	25450.5	0.9989
0.45	25251.1	0.9989	25388.8	0.9991	25494.5	0.9990	25512.0	0.9989
0.50	25273.1	0.9991	25424.0	0.9992	25525.6	0.9991	25572.9	0.9990
0.55	25302.6	0.9991	25398.9	0.9992	25530.6	0.9992	25565.2	0.9990
0.60	25243.2	0.9991	25380.1	0.9993	25490.4	0.9992	25529.7	0.9992
0.65	25262.9	0.9993	25366.1	0.9993	25506.2	0.9994	25517.6	0.9991
0.70	25237.6	0.9993	25384.7	0.9994	25520.8	0.9994	25535.4	0.9992

TABLE I. Continued

$\alpha$	Dopant content, mol %							
	$10^{-4}$		$10^{-3}$		$10^{-2}$		0.1	
	Slope, K <sup>-1</sup>	<i>r</i>	Slope, K <sup>-1</sup>	<i>r</i>	Slope, K <sup>-1</sup>	<i>r</i>	Slope, K <sup>-1</sup>	<i>r</i>
0.75	25276.7	0.9993	25389.1	0.9993	25487.8	0.9994	25538.0	0.9994
0.80	25257.2	0.9994	25407.5	0.9993	25513.7	0.9996	25598.4	0.9994
0.85	25203.7	0.9994	25388.3	0.9994	25530.2	0.9996	25568.6	0.9996
0.90	25239.6	0.9995	25470.2	0.9995	25521.6	0.9996	25603.3	0.9996
0.95	25278.6	0.9996	25422.5	0.9996	25486.7	0.9997	25570.3	0.9998

TABLE II. Values of slope and correlation coefficient obtained for the isoconversional analysis of barium-doped samples of KIO<sub>4</sub> at different dopant concentrations and at different conversions

$\alpha$	Dopant content, mol %							
	$10^{-4}$		$10^{-3}$		$10^{-2}$		0.1	
	Slope, K <sup>-1</sup>	<i>r</i>	Slope, K <sup>-1</sup>	<i>r</i>	Slope, K <sup>-1</sup>	<i>r</i>	Slope, K <sup>-1</sup>	<i>r</i>
0.05	24322.1	0.9996	24355.6	0.9986	24387.2	0.9995	24591.4	0.9987
0.10	24635.0	0.9987	24231.8	0.9982	24313.2	0.9981	24957.9	0.9988
0.15	24808.8	0.9985	24393.3	0.9988	24585.6	0.9989	24832.5	0.9990
0.20	24792.8	0.9987	24530.4	0.9989	24695.4	0.9990	24777.8	0.9991
0.25	24853.0	0.9989	24824.8	0.9992	24966.2	0.9993	24935.0	0.9989
0.30	24912.9	0.9990	24972.3	0.9992	25086.5	0.9993	25104.3	0.9990
0.35	24915.5	0.9989	24975.4	0.9991	25122.0	0.9992	25286.7	0.9993
0.40	25018.1	0.9988	25147.6	0.9993	25289.1	0.9993	25376.4	0.9994
0.45	25081.4	0.9990	25253.6	0.9993	25407.3	0.9995	25467.3	0.9995
0.50	25138.2	0.9989	25373.1	0.9992	25522.9	0.9995	25510.4	0.9995
0.55	25160.2	0.9991	25353.5	0.9990	25518.6	0.9994	25548.6	0.9995
0.60	25175.2	0.9991	25267.4	0.9993	25442.6	0.9995	25507.5	0.9995
0.65	25160.6	0.9992	25162.7	0.9993	25336.4	0.9995	25433.2	0.9994
0.70	25181.1	0.9992	25101.3	0.9993	25201.5	0.9994	25336.5	0.9997
0.75	25238.2	0.9993	25085.0	0.9992	25070.0	0.9994	25333.0	0.9997
0.80	25298.5	0.9996	25091.3	0.9995	25062.3	0.9995	25225.7	0.9997
0.85	25191.5	0.9993	24978.1	0.9995	24962.1	0.9995	25213.7	0.9997
0.90	25092.0	0.9994	24930.0	0.9995	24831.2	0.9993	25320.0	0.9998
0.95	25140.0	0.9994	24890.2	0.9995	24795.8	0.9995	25330.4	0.9997

We found that the apparent activation energy values obtained by the isoconversional method at different conversions ( $\alpha$  range 0.05–0.95 with an interval of 0.05) for sulphate- and barium-doped samples of KIO<sub>4</sub> lie in the range 203–213 kJ mol<sup>-1</sup>. However, in the case of the phosphate- and aluminium-doped samples of KIO<sub>4</sub>, the apparent activation energy values varied only up to 210 kJ mol<sup>-1</sup> from 203 kJ mol<sup>-1</sup>. In the case of untreated KIO<sub>4</sub>, the activation energy value increased from 203 kJ mol<sup>-1</sup> with conversion, passed through a maximum ( $\approx$ 210 kJ mol<sup>-1</sup>), and decreased to the initial value (203 kJ mol<sup>-1</sup>). In all cases, these values are in close agreement with the activation energy values obtained

from the model fitting method ( $206 \pm 3 \text{ kJ mol}^{-1}$ ) using the Prout–Tompkins model.

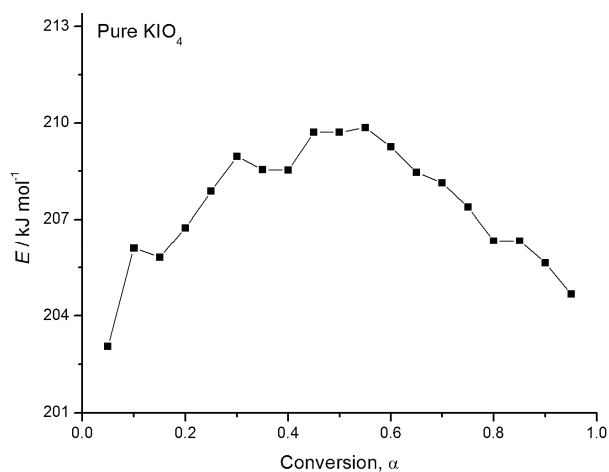


Fig. 4. Plot of the apparent activation energy vs. conversion for pure  $\text{KIO}_4$ .

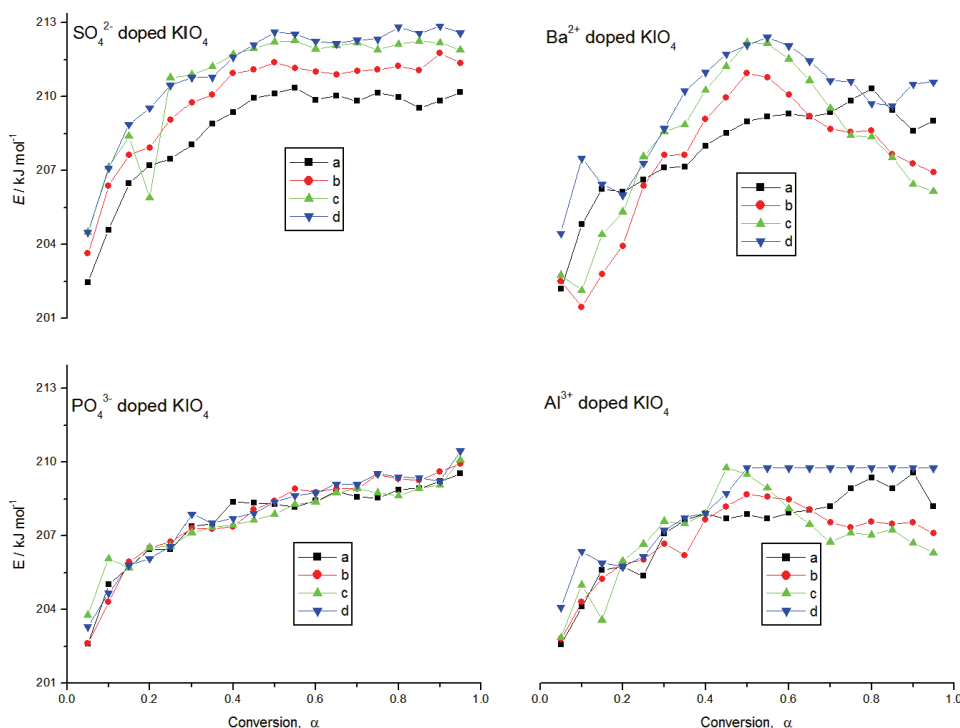


Fig. 5. Plot of the apparent activation energy vs. conversion for sulphate (A), barium (B), phosphate (C) and aluminium (D);  $10^{-4}$  mol %, a,  $10^{-3}$  mol %, b  $10^{-2}$  mol %, c, 0.1 mol %, d.



Perusal of Tables I and II and Figs. 4 and 5 reveals that the deviation of activation energy with conversion is less than  $\pm 2\%$  for all samples of doped and untreated  $\text{KIO}_4$ . This indicates that the thermal decomposition of  $\text{KIO}_4$  proceeds through a single kinetic model, the Prout–Tompkins model, throughout the entire conversion range, as opposed to our previous observation that the acceleration stage was best fitted by the Prout–Tompkins Equation and the decay stage was fitted better by the contracting area equation.<sup>16,19</sup>

#### CONCLUSIONS

The apparent activation energy values obtained previously by model fitting analysis of the isothermal decomposition of untreated and doped samples of  $\text{KIO}_4$  are in good agreement with the present results. The isoconversional studies of the isothermal decomposition of untreated and doped samples of  $\text{KIO}_4$  indicate that the thermal decomposition of  $\text{KIO}_4$  proceeds through a single kinetic model, the Prout–Tompkins model, throughout the entire range of conversion, contrary to our earlier observations.

#### SUPPLEMENTARY MATERIAL

Table S-I and Figs. S-1–S-4 are available electronically at <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

#### ИЗВОД

#### УТИЦАЈ ДОДАТАКА НА ИЗОТЕРМСКУ КИНЕТИКУ РАЗЛАГАЊА КАЛИЈУМ-МЕТАПЕРЈОДАТА

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Изотермска кинетика разлагања калијум-метаперјодата ( $\text{KIO}_4$ ) испитивана је термогравиметријски у функцији концентрације додатака. Термално разлагање се одвија углавном кроз два ступња: период убрзања до  $\alpha = 0,50$  и ступањ разлагања. Термално разлагање  $\text{KIO}_4$  са и без додатака се може описати Prout–Tompkins-овом једначином. Изоконвенционални метод је коришћен у одређивању енергије активације допираних и недопираних узорка. Изоконвенционална испитивања изотермске кинетике нетретираних и допираних  $\text{KIO}_4$  узорака указују на то да се термално разлагање одвија само кроз један кинетички ступањ, Prout–Tompkins модел, у широком опсегу конверзије што је супротно нашим ранијим запажањима.

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#### REFERENCES

1. P. J. Herley, P. W. M. Jacobs, P. W. Levy, *Proc. Roy. Soc.* **318A** (1970) 197
2. V. R. Pai Verneker, K. Rajeshwar, *J. Phys. Chem. Solids* **37** (1976) 63
3. V. A. Benderskii, D. E. Makarov, C. A. Wight, *Chemical Dynamics at Low Temperatures*, Wiley, New York, 1994, p. 385
4. M. E. Brown, D. Dollimore, A. K. Galwey, *Reactions in the Solid State, Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1980, p. 340

5. T. B. Brill, K. J. James, *Chem. Rev.* **93** (1993) 2667
6. J. H. Flynn, in *Encyclopedia of Polymer Science and Engineering*, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, Eds., Wiley, New York, 1989, p. 690
7. J. Sestak, *Thermophysical Properties of Solids*, in *Comprehensive Analytical Chemistry Vol. XIID*, Elsevier, Amsterdam, 1984, p. 440
8. J. G. Fatou, in *Encyclopedia of Polymer Science and Engineering*, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, Eds., Wiley, New York, 1989, p. 231
9. A. K. Galwey, *Thermochim. Acta* **413** (2004) 139
10. D. Dollimore, *Chem. Rev.* **68** (1996) 63
11. M. P. Kannan, *J. Thermal. Anal.* **32** (1987) 1219
12. K. Muraleedharan, M. P. Kannan, *React. Kinet. Catal. Lett.* **39** (1989) 339
13. M. P. Kannan, K. Muraleedharan, *Thermochim. Acta* **158** (1990) 259
14. T. Gangadevi, M. P. Kannan, B. Hema, *Thermochim. Acta* **285** (1996) 269
15. M. P. Kannan, T. Gangadevi, *Thermochim. Acta* **292** (1997) 105
16. K. Muraleedharan, M. P. Kannan, *Thermochim. Acta* **359** (2000) 161
17. M. P. Kannan, V. M. Abdul Mujeeb, *React. Kinet. Catal. Lett.* **72** (2001) 245
18. K. Muraleedharan, M. P. Kannan, T. Gangadevi, *J. Therm. Anal. Cal.* **100** (2010) 177
19. K. Muraleedharan, M. P. Kannan, T. Gangadevi, *Thermochim. Acta* **502** (2010) 24
20. O. N. Breusov, N. J. Kashina, T. V. Rezvina, *Zh. Neorg. Khim.* **15** (1970) 612
21. P. Bianco, R. Subbah, G. Perinet, *Bull. Soc. Chim.* **9** (1967) 3437
22. J. G. Hooley, *Can. J. Chem.* **35** (1957) 374
23. S. Vyazovkin, C. A. Wight, *Annu. Rev. Phys. Chem.* **48** (1997) 125
24. E. G. Prout, F. C. Tompkins, *Trans. Faraday Soc.* **40** (1944) 488
25. B. R. Philips, D. Taylor, *J. Chem. Soc.* (1963) 5583
26. R. A. W. Hill, *Trans. Faraday Soc.* **54** (1958) 685
27. M. M. Markowitz, D. A. Boryta, *J. Phys. Chem.* **65** (1961) 1419
28. K. H. Stern, *High Temperature Properties and Thermal Decomposition of Inorganic Salts with Oxyanions*, CRC Press, Boca Raton, FL, 2001
29. A. K. Galwey, M. E. Brown, *Thermal Decomposition of Ionic Solids, Studies in Physical and Theoretical Chemistry*, Vol. 86, Elsevier, Amsterdam, 1999
30. F. Solymosi, *Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase*, Wiley, London, 1977.