

## Thermal Decomposition of $\text{KIO}_4$ and $\text{NaIO}_4$ in Relation to Solid-state Isotopic Exchange Reactions

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The thermal decomposition of  $\text{KIO}_4$  and  $\text{NaIO}_4$  has been studied. The decomposition product,  $\text{KIO}_3$  or  $\text{NaIO}_3$ , suffers a very efficient exodiffusion during heating in such a way that the partly decomposed crystals consist of two parts: the outer part is a fragile layer of almost pure iodate, while the inner part is a solid crystalline lattice of almost pure periodate. The dimensions of the latter are not affected by the decomposition, so that its density decreases in proportion to the decomposed fraction. The decomposition isotherms present a saturation at long heating times which is not due to atmospheric effects, but is suppressed when the heating is performed with continuous removal of the outer layer. Kinetic analysis of the data shows a remarkable continuity between the exchange process, occurring at lower temperatures, and the decomposition. In particular, the dimensionality of the reaction,  $n$ , from the Erofeev equation, ranges in  $\text{KIO}_4$  roughly from 1 to 2 with increasing temperature in the former case, then from 2 to 3 in the latter. These values are systematically higher by one unit in  $\text{NaIO}_4$ , indicating that the nucleation process, which creates the driving defect, cannot be neglected as it can for  $\text{KIO}_4$ . Both exchange and decomposition are dominated by the exodiffusion of some combined vacancy type defect, promoting the exodiffusion of the iodate and eventually triggering the decomposition; at sufficiently high temperature, the latter process becomes autocatalytic and develops three-dimensionally ( $n = 3$  or 4).

In spite of numerous studies, the mechanisms of isotopic exchange reactions in solids are poorly understood.<sup>1</sup> According to the various models proposed so far, two major routes to the achievement of exchange may be considered in doped matrices: (i) the release and movement of charges, either electrons<sup>2,3</sup> or holes,<sup>4,5</sup> captured at the site of the dopant; (ii) the creation and movement of defects in the lattice.<sup>6–8</sup> The involvement of mobile charges is likely when the solids are irradiated prior to the thermal treatments, while the involvement of defects is plausible when exchange is observed at relatively high temperatures. The nature of the defects involved in the latter case seems to be variable and would range from simple cation<sup>6,9</sup> or anion<sup>7,10</sup> vacancies to larger structural defects, such as when the exchange occurs concurrently with dehydration<sup>11</sup> or decomposition<sup>12,13</sup> processes.

In previous papers<sup>14,15</sup> we have studied isotopic exchange in alkali-metal periodate matrices doped with  $\text{IO}_3^-$  ions by precipitation from hot solutions. These experiments were largely prompted by the remarkable similarities observed between isotopic exchange isotherms of  $\text{I}^-$ -doped  $\text{KIO}_4$ <sup>16</sup> and the decomposition isotherms of the matrix.<sup>17</sup> In either case, plateaux appear at long heating times, which seemed a promising clue to the mechanism of exchange. The main information derived on the thermally activated exchange was as follows: (i) exchange is observed in the isomorphous, tetragonal, Na, K and Rb periodates, not in orthorhombic  $\text{CsIO}_4$ ; in each case, exchange begins *ca.* 100 K below the temperature at which macroscopic decomposition

is initiated (*ca.* 473 K). (ii) In  $\text{KIO}_4$ , a very efficient exodiffusion of the dopants is observed concomitantly to the exchange while in  $\text{NaIO}_4$  this occurs only above 473 K. (iii) All isotherms show a saturation in the exchanged fraction at long heating times. (iv) The overall process would be dominated by the exodiffusion of a vacancy type defect able to promote the exodiffusion of the iodate ions. The kinetic parameters are strongly correlated with macroscopic lattice parameters, including the packing coefficient, which allows us to compare the ease of formation and movement of defects in the matrices studied.

In this paper, the decomposition of  $\text{KIO}_4$  and  $\text{NaIO}_4$  is studied in order to gain more information on the possible relationships with the exchange process.

## Experimental

The samples of  $\text{KIO}_4$  were prepared in the same way as in the exchange study,<sup>14,15</sup> by rapid chilling of hot solutions in liquid nitrogen. Anhydrous  $\text{NaIO}_4$  was obtained by precipitation from a hot (363 K) saturated solution<sup>14</sup> in a water bath at 313 K.

The analytical method, based on solvent extraction of  $\text{I}^-$  followed by double precipitation of  $\text{IO}_3^-$  has been described previously.<sup>14</sup> The fraction decomposed,  $D$ , was determined by weighing the  $\text{AgIO}_3$  precipitate after it had been washed and dried. As no reduced form was found at any temperature, we define  $D = N(\text{IO}_3^-)/N^0(\text{IO}_4^-)$ , the ratio of the number of moles of iodate after heating to that of periodate before heating. The average error on  $D$  was within 0.6 abs. %.

The density measurements were made using a 3 cm<sup>3</sup> pycnometer with toluene as reference, for which we found a density of 0.834 g cm<sup>-3</sup> at 291 K.

Heating in air was conducted as previously,<sup>15</sup> using either a thermostatically controlled oil bath with a thermal stability within 0.5 K (up to 573 K), or a cylindrical oven with a stability within 1 K (above 573 K). For heating *in vacuo*, the samples were introduced into a Pyrex tube (1 cm diameter, 14 cm length). The tube was evacuated, then immersed in a metallic tube containing hot silicone oil and placed axially in the cylindrical oven in a vertical position. After heating, the oven and tube were swiftly taken away as pumping was stopped, and the sample was cooled in liquid nitrogen.

## Results

### The Decomposition Process and the Role of Oxygen

Fig. 1 shows the isochronal variation of  $D$  in  $\text{KIO}_4$  for 2 h heating in air, and fig. 2 shows the isothermal curves:  $D$  levels off at long heating times, at all temperatures. No significant increase in  $D$  is found with extended heating: *e.g.* heating for 3, 68 and 72 h at 553 K yields 54.3, 54.4 and 53.2% for  $D$ , respectively. Also, the plateaux do not result from a reversible process, as slow cooling after a plateau is reached does not induce any decrease in  $D$ . Thus, 3 h at 548 K then at 543 K gives 40.1 and 40.8%, respectively, and 3 h at 563 K, then at 558 K gives 70.2 and 70.5%, respectively. Conversely, increasing the temperature from  $T_1$  to  $T_2$  after a plateau is reached at  $T_1$  leads to the plateau value characteristic of  $T_2$ . For instance, 3 h heating at 543 K, then at 553 and 563 K increases  $D$  from 20.4 to 51.5 then 70.5%, respectively, as compared to 52.4 and 70.2% obtained when heating for 3 h at 553 and 563 K, respectively.

As the presence of plateaux initially suggested the presence of some equilibrium involving the oxygen, isothermal heating was carried out *in vacuo*. As shown in fig. 3,  $D$  increases to 100% at all temperatures, in contrast to what is observed in air. However, heating carried out under oxygen shows no effect of the atmosphere. For example, 3 h at 543 K under 1.23 atm†  $\text{O}_2$  gives  $D = 21.0\%$  as compared to 20.5% in

† 1 atm = 101325 Pa.

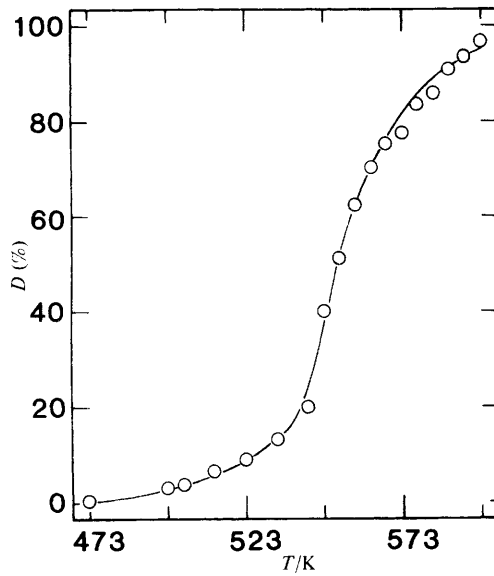


Fig. 1. Isochronal (2 h) variation of the decomposed fraction,  $D(\%)$ , in  $\text{KIO}_4$  heated in air.

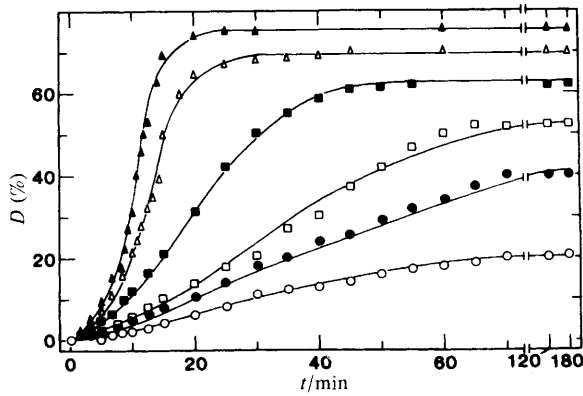


Fig. 2. Isothermal variation of the decomposed fraction  $D(\%)$ , in  $\text{KIO}_4$  heated in air at:  $\circ$ , 543;  $\bullet$ , 548;  $\square$ , 553;  $\blacksquare$ , 558;  $\triangle$ , 563 and  $\blacktriangle$ , 573 K.

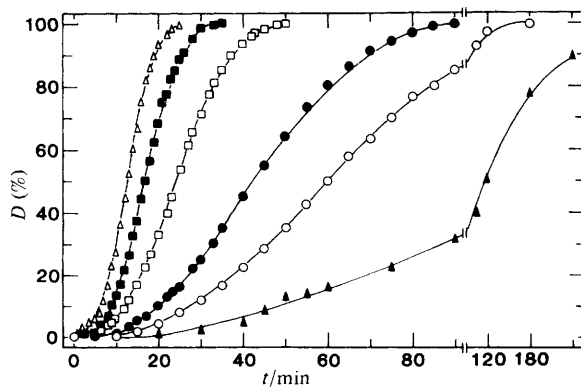


Fig. 3. Isothermal variation of the decomposed fraction,  $D(\%)$ , in  $\text{KIO}_4$  heated *in vacuo* at:  $\blacktriangle$ , 543;  $\circ$ , 548;  $\bullet$ , 553;  $\square$ , 558;  $\blacksquare$ , 563 and  $\triangle$ , 573 K.

## Solid-state Isotope Exchange

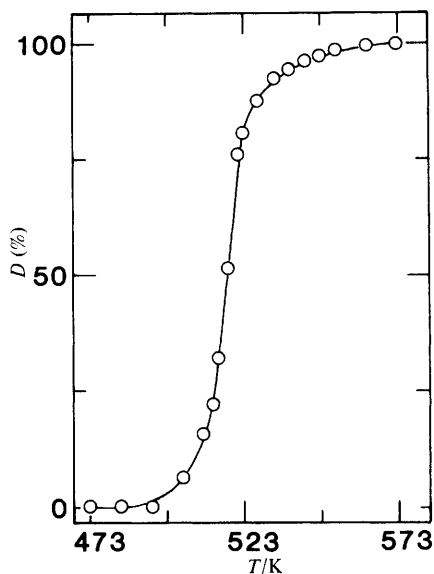


Fig. 4. Isochronal (2 h) variation of the decomposed fraction,  $D$  (%), in  $\text{NaO}_4$  heated in air.

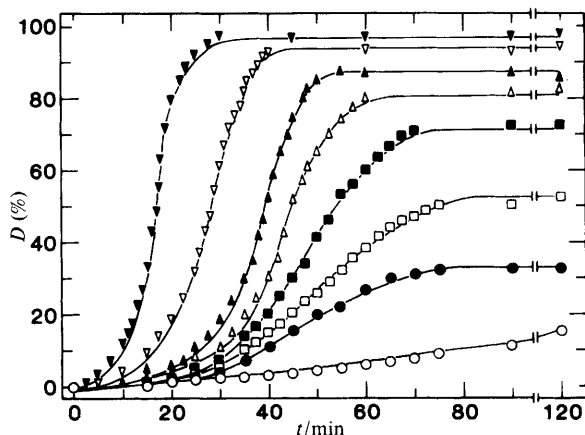


Fig. 5. Isothermal variation of the decomposed fraction,  $D$  (%), in  $\text{NaIO}_4$  heated in air at:  $\circ$ , 510;  $\bullet$ , 515;  $\square$ , 518;  $\blacksquare$ , 521,  $\triangle$ , 523;  $\blacktriangle$ , 528;  $\nabla$ , 538 and  $\blacktriangledown$ , 548 K.

air, and 3 h at 553 K under 1.55 atm  $\text{O}_2$  gives 51.2% compared to 52.3% in air. The effect of heating *in vacuo*, shown to be purely mechanical, is discussed later on.

Fig. 4 shows the isochronal (2 h) variation of  $D$  in  $\text{NaIO}_4$ . By comparison with  $\text{KIO}_4$ , the slope of the sigmoid is steeper, indicating a higher degree of development. Fig. 5 shows the isothermal curves, each displaying a plateau, as in  $\text{KIO}_4$ . Heating *in vacuo* allows the reaction to proceed steadily, up to 100%, as shown in fig. 6.

### Distribution of the Decomposed Fraction

To understand better how decomposition develops, chemical analyses have been performed as a function of the distance from the surface of the  $\text{KIO}_4$  crystals by successive dissolution of the samples in 1.2  $\text{cm}^3$  of cold (278 K) water. The layers thus obtained represent 1% of the total volume of the crystals.<sup>14</sup> Results are presented in

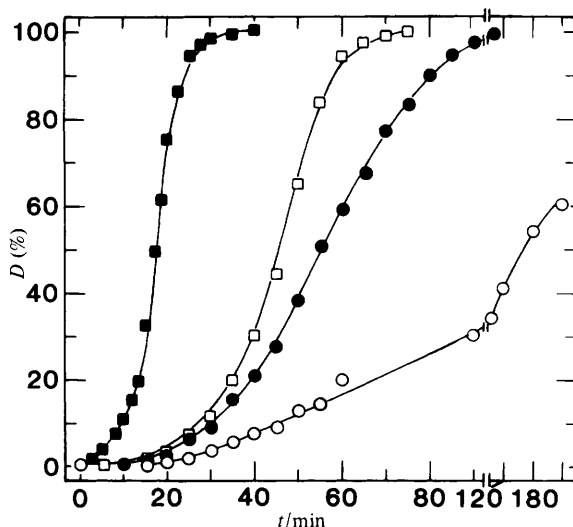


Fig. 6. Isothermal variation of the decomposed fraction,  $D(\%)$ , in  $\text{NaIO}_4$  heated *in vacuo* at:  $\circ$ , 510;  $\bullet$ , 518;  $\square$ , 523 and  $\blacksquare$ , 548 K.

Table 1. Distribution of the decomposed fraction as a function of the number of layer from the surface,  $N$ , after 60 min heating at 553 K ( $D_1$ ) and after 10 min at 563 K ( $D_2$ ) in  $\text{KIO}_4$

$N$	$D_1(\%)$	$D_2(\%)$	$R_1(\%)$	$R_2(\%)$
1	47.8	13.2	95.2	61.6
2	1.8	3.0	3.6	13.9
3	0.6	1.6	1.2	7.4
4	0.0	0.9	0	4.2
5	0	ca. 0	0	0

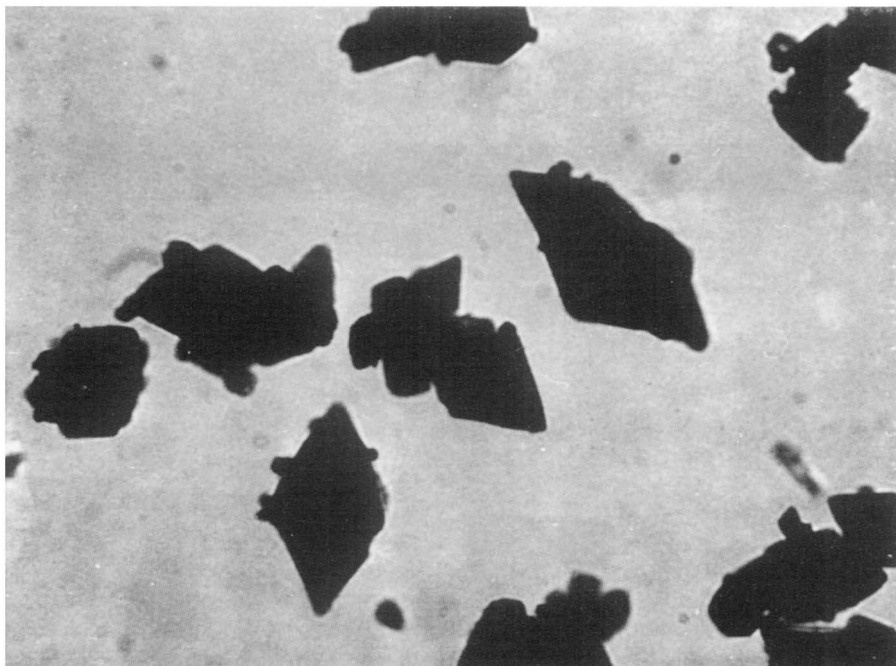
$R_1$  and  $R_2$  are the ratios of  $D_1$  and  $D_2$  to the total decomposed fraction,  $D$  (50.2 and 21.6%, respectively).

table 1 when the plateau is reached and in the acceleratory part of an isotherm. In either case, most of the decomposed fraction lies in the outer layer of the crystals.

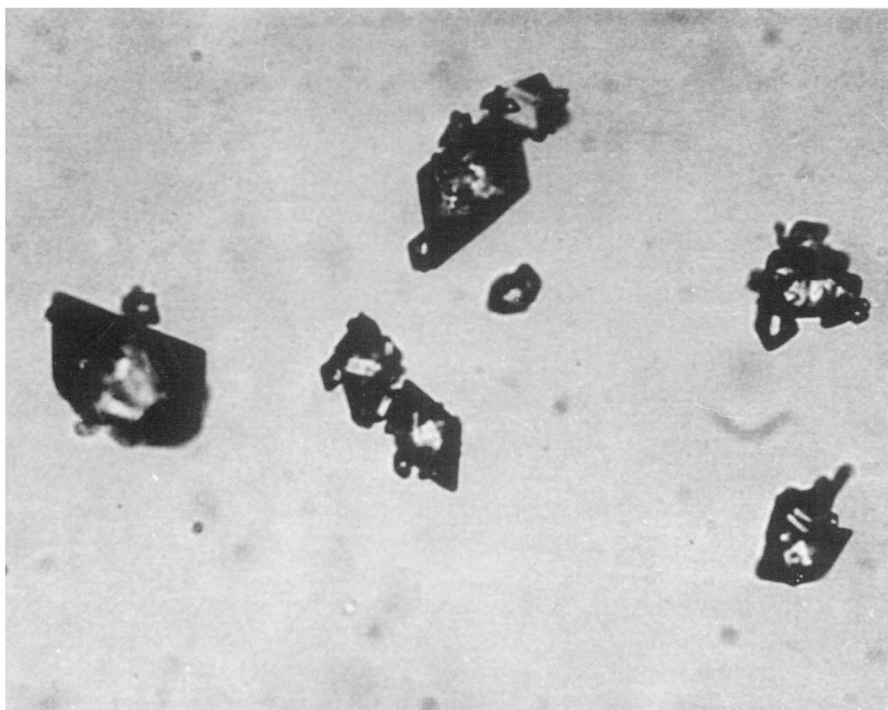
A similar study was made on  $\text{NaIO}_4$ . As shown in fig. 7, the fraction of total  $\text{NaIO}_3$ ,  $P_d$ , reaching the surface for a fixed  $D$  value increases with temperature. The isothermal variations of  $P_d$  are similar to those observed for the iodate dopants in  $\text{KIO}_4$ .<sup>15</sup>

The arrangement of the two regions of the crystals has been further assessed by sieving with the same meshes as used to select the initial samples (*i.e.* 45–53  $\mu\text{m}$ ). It appears that the heated crystals of either  $\text{KIO}_4$  or  $\text{NaIO}_4$  effectively consist of two parts: an external, powdery layer which passes through the sieve (fraction A), and an inner, crystalline part (fraction B). Fraction A includes most of the iodate, in such a way that a close estimate of  $D$  can be made just by sieving. In  $\text{KIO}_4$  for example, after 2 h heating at 553 K, fraction A represents 50% of the initial weight of the samples and contains 93.5% of the  $\text{KIO}_3$ , while the  $D$  value determined by chemical analysis is 52.1%. Similarly, fraction A constitutes 20% of the initial weight after 2 h at 543 K, with  $D = 19.7\%$ .

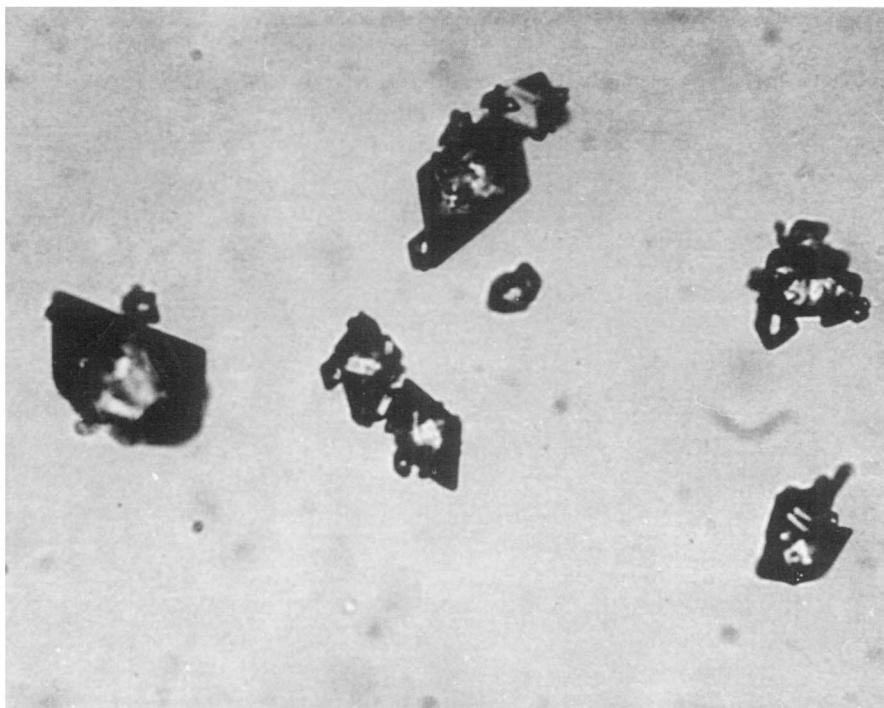
An amazing result is therefore that the crystallites of fraction B, practically pure



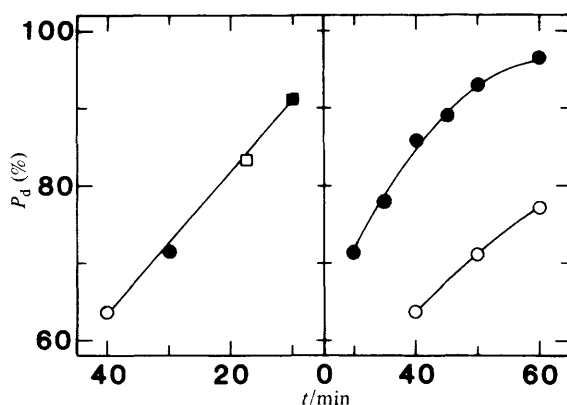
**Plate 1.** Photomicrograph of partly decomposed  $\text{KIO}_4$  crystals (120 min at 573 K;  $D = 76.8\%$ ), not sieved. Enlargement: *ca.* 325.



**Plate 2.** Same as fig. 8, sieved (the outer iodate layer is removed).



**Plate 3.** Photomicrograph of partly decomposed  $\text{KIO}_4$  crystals (60 min at 553 K;  $D = 50.2\%$ ), sieved. Enlargement: *ca.* 325.



**Fig. 7.** Variation of the fraction of iodate from decomposition,  $P_d$ (%), in the external, separable layer of heated crystals of  $\text{NaIO}_3$ : (left) for various temperatures and times, when the total decomposed fraction is constant ( $D \approx 11\%$ ); (right) as a function of time at two temperatures.

○, 515; ●, 523; □, 538 and ■, 548 K.

**Table 2.** Distribution of the size of the crystallites in various samples of  $\text{KIO}_4$ : (a) sieved untreated; (b) sieved after 1 h at 553 K; (c) sieved after 2 h at 573 K; (d) same as (c), but not sieved

size/ $\mu\text{m}$	a(%)	b(%)	c(%)	size/ $\mu\text{m}$	d(%)
45	5.4	5.0	6.1	54	4.5
46	9.0	8.8	8.2	55	6.1
47	19.4	15.2	16.7	56.5	8.0
48	10.5	9.3	13.2	58	9.4
49	13.7	11.7	9.4	60	29.5
50	26.9	30.9	29.0	63	11.8
51	8.2	9.2	5.2	65	6.1
52	5.4	6.5	6.0	67.5	6.3
53	1.5	5.0	5.1	69	7.5
55	0	1.4	1.1	70	10.8

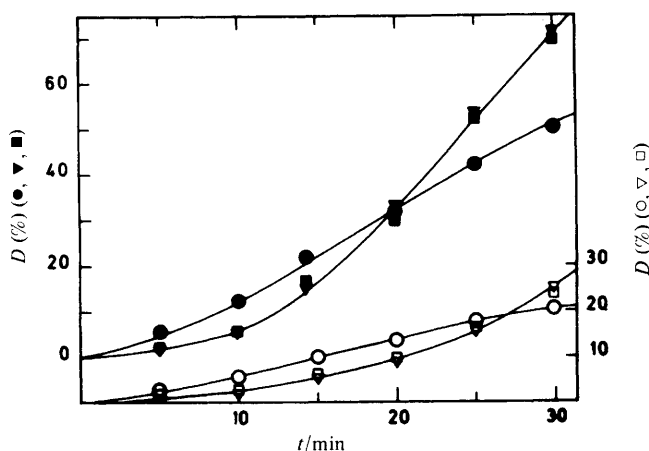
periodate, preserve their size even though they have lost a large portion of their mass. This is illustrated for  $\text{KIO}_4$  in table 2 which shows that the micrometrically determined size of these crystallites is the same as that in the untreated samples,  $50 \mu\text{m}$ ,<sup>14</sup> even with  $D$  as high as 50.2% (1 h at 553 K) or 76.8% (2 h at 573 K). Microscopic examination of the samples shows that after heating for 2 h at 573 K, the crystals are opaque, with a size of  $60 \mu\text{m}$  (see plate 1). Once cleared of the external  $\text{KIO}_3$  layer, they display the same crystalline aspect and crystal size,  $50 \mu\text{m}$ , as before heating (plates 2 and 3). Note that assimilating the crystals of fraction A to spheres of a radius of  $50 \mu\text{m}$  and taking fractions A and B as pure  $\text{KIO}_3$  and  $\text{KIO}_4$ , respectively, with  $D = 76.8\%$ , the expected total radius of the decomposed crystals is  $59 \mu\text{m}$ , in close agreement with the experimental size.

The preservation of the inner crystal size has dramatic consequences on its density, which varies from  $d_1 = 3.56$  to  $d_2 = 1.78$  and  $d_3 = 0.858 \text{ g cm}^{-3}$ , when  $D$  changes from 0 to 50.2 and 76.8%, respectively. The ratio of the densities correlates well with that of the non-decomposed fractions ( $p = 100 - D$ ), with  $d_1/d_2 = 2.00$  for  $p_1/p_2 = 2.01$  and  $d_1/d_3 = 4.14$  for  $p_1/p_3 = 4.31$ .



**Table 3.** Isothermal variation of the decomposed fraction in  $\text{KIO}_4$ , at 553 K:  $D_1$ , initial sample;  $D_2$ , the same, heated for 30 min at 553 K, then sieved

$t/\text{min}$	$D_1(\%)$	$D_2(\%)$
15	10.1	11.4
30	20.7	25.4
45	37.3	43.2
60	50.2	58.5
120	52.1	61.1



**Fig. 8.** Isothermal variation of the decomposed fraction,  $D(\%)$ , in  $\text{KIO}_4$  heated in air without ( $\circ$ ) and with ( $\square$ ) continuous agitation, and *in vacuo* ( $\nabla$ ). Open symbols, at 553 K; closed symbols, at 558 K.

### Role of the Interface between the Outer and Inner Parts of the Heated Crystals

The existence of two parts in the heated crystals prompted us to study the specific thermal behaviour of the inner part, which is chemically and geometrically similar to the initial crystals. Table 3 shows the isothermal variation of  $D$  in two batches of  $\text{KIO}_4$ . Batch 1 is the originally precipitated salt and batch 2 is the same after 30 min heating at 553 K followed by sieving to eliminate the iodate layer. In both cases  $D$  reaches a maximum (at a higher value in batch 2) which cannot be attributed to any difference in the crystal sizes.

It thus appears that removing the outer iodate layer allows decomposition, development of which had previously ceased, to start again. This is confirmed by the following: a freshly prepared sample of  $\text{KIO}_4$  was heated 3 successive times for 2 h at 543 K. After the first and second heatings, the sample was sieved, causing the complete loss of iodate and of 1.5 and 9.7% of the remaining  $\text{KIO}_4$ , respectively, which passes through the sieve. The successive plateau values are  $D = 19.7$ , 23.8 and 38.9%. These results show that the role of the vacuum (fig. 3) is not related to any effect of the atmosphere. In particular, visual observation of the samples during heating *in vacuo* shows that the oxygen from decomposition is rapidly expelled from the crystals; the powdery outer layer is thus continuously removed and accumulates at the bottom of the vessel. As illustrated in fig. 8, this purely mechanical effect is verified by comparing the

**Table 4.** Fitting parameters derived for the isotherms on the basis of eqn (1) for heating in air and under vacuum

T/K	air			vacuum		
	$k/s^{-1}$	$n$	$\sigma(\%)$	$k/s^{-1}$	$n$	$\sigma(\%)$
			KIO <sub>4</sub>			
543	0.026	1.7	0.55	0.007	2.1	0.19
548	0.023	1.6	1.15	0.014	2.5	0.19
553	0.025	1.9	1.96	0.020	2.5	0.50
558	0.042	1.8	0.78	0.036	2.8	0.28
563	0.069	2.7	2.08	0.052	3.0	0.32
573	0.083	2.8	2.12	0.069	3.0	0.36
			NaIO <sub>4</sub>			
510	0.011	2.5	0.37	0.009	1.95	1.22
515	0.020	3.6	0.56	—	—	—
518	0.018	3.5	0.62	0.016	3.3	0.96
521	0.019	4.1	0.95	—	—	—
523	0.022	4.9	1.57	0.020	4.6	2.03
528	0.025	5.2	2.44	—	—	—
538	0.033	4.2	2.12	—	—	—
548	0.055	4.0	2.75	0.054	3.9	2.55

decomposed fractions obtained *in vacuo* and in air with and without continuous agitation of the samples to remove the iodate layer:  $D$  increases steadily to 100% in the same way in the two first cases, while it levels off in air.

Similar phenomena are observed with NaIO<sub>4</sub>. A sample was heated three successive times at 518 K for 2 h at the plateau (fig. 5), then sieved. The first heating leads to  $D = 50.2\%$ , and only 1.5% of the NaIO<sub>4</sub> passes through on sieving. The two next heatings give  $D = 35.8$  and 27.4%, respectively, with less than 0.5% of NaIO<sub>4</sub> lost after each sieving. The existence of an external, fragile layer is thus confirmed, but the plateau value decreases after each heating run while it increases in KIO<sub>4</sub>.

### Data Analysis

As was the case for the exchange data,<sup>15</sup> the various expressions proposed in the literature to describe the variation of  $D$  with time,  $t$ , do not include the possibility of plateaux in the isotherms,<sup>18–20</sup> still less that of a strong exodiffusion of the decomposition product. Several models tentatively applied to our data, such as the branching or the Mampel models,<sup>19</sup> were shown to be inadequate. To compare the kinetics of decomposition in air and *in vacuo* and those of exchange,<sup>15</sup> only results based on the Erofeev equation<sup>20,21</sup> will be discussed. As previously,<sup>15</sup> comparison of the quality of fit may be made through the average deviation,  $\sigma$ , which, in favourable cases, should be close to the experimental error on  $D$ , *i.e.* *ca.* 0.6%. The solid lines in fig. 2–6 are calculated from the parameters derived without any constraints (see table 4). The Erofeev expression is as follows:

$$D = D_{\infty} \{1 - \exp[-(kt)^n]\} \quad (1)$$

where  $D_{\infty}$  is introduced to take account of the plateau value of  $D$ ;  $n = m + p(2)$  expresses the overall dimensionality of the reaction, including both nucleation (*e.g.*  $p = 0$  for pre-existing nuclei) and the mode of development (*e.g.*  $m = 3$  for a three-dimensional propagation).

**Table 5.** Isothermal variation of  $D$ (%) in  $\text{KIO}_4$ : (a) pure, (b) doped with 630 ppm  $\text{IO}_3^-$ , (c) doped with 600 ppm  $\text{I}^-$

$T/\text{K}$	$t/\text{min}$	$D(a)$ (%)	$D(b)$ (%)	$D(c)$ (%)
553	30	20.7	21.8	20.0
	60	50.2	49.7	48.1
	90	51.6	51.8	50.8
563	30	68.1	69.7	67.9
	60	70.0	70.6	69.3
	90	70.8	70.8	69.9

Table 4 shows the parameters derived when fitting eqn (1) to the data. Analysing the isotherms separately gives very good fits of the data on  $\text{KIO}_4$  *in vacuo*, for which  $D_x = 100\%$  at all temperatures, while the agreement is only reasonable for the other data.

Globally, eqn (1) is not adequate: (i) the quality of fit is only mediocre in several cases. (ii) The value of  $n$  changes with temperature, roughly from 2 to 3 between 543 and 573 K for  $\text{KIO}_4$  and from 3 to 4 between 510 and 548 K for  $\text{NaIO}_4$ . This variation is significant: with  $\text{KIO}_4$  for instance, fixing the value of  $n$  results in an increase of  $\sigma$  from 0.78% ( $n = 1.8$ , table 4) to 1.1% ( $n$  fixed at 2) and 4.1% ( $n = 3$ ) for the isotherm at 558 K in air. Similarly,  $\sigma$  goes from 0.19% ( $n = 2.5$ , table 4) to 3.6% ( $n = 2$ ) and 2.9% ( $n = 3$ ) at 548 K *in vacuo*. Furthermore, fitting the isotherms in air for  $\text{KIO}_4$  (or  $\text{NaIO}_4$ ) in successive slices of increasing time also shows an increase of  $n$  with time, roughly from  $n = 1.5$  (or 3) in the initial part to  $n = 3$  (or 5) in the decay region. (iii) No reasonable Arrhenius plot can be drawn from the values of the decomposition rate constant,  $k$ . As a consequence, no satisfactory fit can be obtained when fitting all isotherms together on the basis of eqn (1) with  $k = k^\circ \exp(-E/kT)$ . (iv) The plateau value,  $D_x$ , is arbitrarily introduced into eqn (1).

Nevertheless, the increase of  $n$  with temperature is instructive, strongly suggesting a progressive change in the development of the decomposition reaction from a low-dimensional to a three-dimensional mode. In particular, the latter appears to be largely dominant when heating *in vacuo*.

## Discussion

The decomposition process is complex. As for the exchange,<sup>15</sup> the driving process is probably the diffusion of a vacancy-type defect responsible for both exodiffusion of the iodate and for the propagation of the decomposition. The existence of the plateaux would thus be due to the trapping of this defect at surface sites and, as soon as some iodate has accumulated on the surface, to its penetration into the building outer layer, acting as a more efficient trap. That decomposition starts again upon removal of this layer betrays the existence of an equilibrium at the interface, strongly displaced towards the layer to result in a low concentration of the driving defects in the core and thereafter in the maximisation of the decomposition. Continuous rupture of this equilibrium by agitation or by the sudden expulsion of the oxygen, under vacuum, suppresses the saturation effect (fig. 3, 6 and 8). Note that the presence of plateaux in  $\text{NaIO}_4$  exchange isotherms at temperatures where no exodiffusion of  $\text{Na}^{131}\text{IO}_3$  is seen,<sup>15</sup> and their absence in the decomposition isotherms when the surface of the crystals is kept clean implies that the trapping efficiency of the surface decreases with increased temperature and underlines the important role of the outer iodate layer.

The values of  $n$ , in the Erofeev equation, which reflect the steepness of the slopes of the isochronal or isothermal sigmoids, and their variation with temperature are quite instructive. In  $\text{KIO}_4$ , the dimensionality roughly increases from 1 to 2 between 373 and 473 K when exchange occurs, then from 2 to 3 between 543 and 573 K when decomposition is effective. Confirming this continuity between the two processes,  $n$  varies from *ca.* 2 at 423 K in the exchange region for  $\text{NaIO}_4$  (with a drop to  $n \approx 1$  at 493 K), then increases from 3 to 5 in the decomposition region between 510 and 528 K (with a further decrease to 4 at 548 K; table 4). In all cases,  $n$  appears to be higher by 1 or 2 units in  $\text{NaIO}_4$  than in  $\text{KIO}_4$ , indicating that nucleation, in terms of energy and mode of formation of the nuclei, is not a negligible process in the former case as compared to the latter. This difference also appears when decomposition is carried out *in vacuo*, with  $n$  rapidly tending to 3 in  $\text{KIO}_4$  when temperature increases, and to *ca.* 4 in  $\text{NaIO}_4$  (table 4). Values of  $n$  close to 1 reflect a reaction triggered by the simple diffusion of a defect. Conversely,  $n = 3$  suggests an autocatalytic, explosive process propagating in a three-dimensional mode, with a low formation energy of the driving defect [see eqn (2)]. Several observations indicate that the latter is very probably a combined defect as that promoting the initial exchange upon precipitation of the samples:<sup>14</sup> (i) the role of extrinsic defects is ruled out as no significant difference is found in isotherms for  $\text{KIO}_4$  (either pure or doped with  $\text{IO}_3^-$  or  $\text{I}^-$ ) (table 5); (ii) values of  $n$  lower than 2 (table 4) imply that the nature of the driving defect must be different from that of the defect(s) produced by the local decomposition reaction; otherwise, the propagation is autocatalytic and  $n = 3$ ; (iii) the exodiffusion concerns the whole iodate molecule and is very efficient since even when decomposition is not well advanced, the proportion of iodate in the crystal core is very low (table 1). This implies the possibility of large movements in the lattice.

On this basis, the propagation of the decomposition can be explained if the driving defect brings about sufficient changes in the vibrational modes of the ligands at a nearby anion site of the lattice, eventually resulting in bond rupture. At low temperatures, this will occur casually along the diffusion path of this defect on its way to the surface ( $n = 1$ ). At high temperatures, the density of the decomposition sites increases and the defects produced at each site have a greater opportunity to combine, leading to the formation of a new driving defect:  $n$  tends to 3.

Finally, as was the case for exchange in the various alkali-metal periodates,<sup>2</sup> a good correlation appears when comparing the developments of decomposition in  $\text{KIO}_4$  and in  $\text{NaIO}_4$  and the packing coefficients,  $f_c$ , which reflect the ease of formation and movement of defects in these matrices. In  $\text{KIO}_4$ , where  $f_c = 46.8\%$ , the onset of decomposition occurs at a lower temperature ( $T_D = 473 \text{ K}$ )<sup>2,3</sup> than in  $\text{NaIO}_4$  ( $f_c = 50.8\%$ ,  $T_D = 493 \text{ K}$ ), showing that the driving defect is created more easily. However, this defect is also more mobile than in  $\text{NaIO}_4$ , with a resulting more efficient exodiffusion and a subsequent faster exodiffusion of the iodate. As a consequence, the plateau values reached by  $D$  at each temperature are relatively lower and the process expands over a larger temperature range in  $\text{KIO}_4$  than in  $\text{NaIO}_4$ .

## Conclusion

The present work shows that the decomposition process in  $\text{KIO}_4$  and  $\text{NaIO}_4$  is complex. In continuity with previous conclusions on isotopic exchange in this matrix, the overall reaction would be dominated by the exodiffusion of a specific, very probably combined defect, able to trigger decomposition and also to promote the exodiffusion of the decomposition product.

These findings provide for the first time a basic scheme for the exchange mechanism which appears to be strongly correlated with that of decomposition. In particular, a simple, sound explanation is given for the presence of plateaux in the isotherms, as are

very often observed in hot-atom and solid-state isotopic exchange chemistry. Undertaking similar studies as on the periodates on other systems would be very important as to the possible generalization of the concepts developed here.

Further work is obviously needed for a better understanding of the complex processes involved. Physical techniques, such as conductivity or positron annihilation, might provide useful information on the physico-chemical states of the matrices before and after decomposition has begun. It would be particularly interesting to study the properties of the low-density, crystalline core of the partly decomposed periodate crystals.

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## References

- 1 G. Duplâtre, in *Hot Atom Chemistry*, ed. T. Matsuura (Kodansha, Tokyo, 1984), p. 201.
- 2 A. Nath, S. Khorana, P. K. Mathur and S. Sarup, *Indian J. Chem.*, 1966, **4**, 51.
- 3 M. Kalliat and A. Nath, *J. Inorg. Nucl. Chem.*, 1981 **43**, 271.
- 4 C. H. Collins, K. E. Collins, Y. F. Ghos and D. J. Apers, *Radiochim. Acta*, 1965, **4**, 211.
- 5 T. Costea, I. Negoescu and F. Podeanu, *Radiochim. Acta*, 1970, **14**, 87.
- 6 S. F. Fernandez-Valverde, G. Duplâtre and A. G. Maddock, *J. Inorg. Nucl. Chem.*, 1978, **40**, 999.
- 7 R. Bell, K. Rössler, G. Stöcklin and S. R. Upadhyay, *J. Inorg. Nucl. Chem.*, 1972, **34**, 461.
- 8 E. Lazzarini and A. L. Fantola-Lazzarini, *J. Inorg. Nucl. Chem.*, 1975, **37**, 407.
- 9 S. M. Fernandez-Valverde and G. Duplâtre, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2825.
- 10 G. B. Schmidt and K. Rössler, *Radiochim. Acta*, 1966, **5**, 123.
- 11 E. Lazzarini and A. L. Fantola-Lazzarini, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1233.
- 12 E. Lazzarini and A. L. Fantola-Lazzarini, *J. Inorg. Nucl. Chem.*, 1976, **38**, 657.
- 13 G. Albarran, C. Archundia and A. G. Maddock, *Radiochim. Acta*, 1982, **30**, 199.
- 14 S. Takriti and G. Duplâtre, *Radiochim. Acta*, 1987, **42**, 179.
- 15 S. Takriti and G. Duplâtre, *Radiochim. Acta*, 1988, **43**, 45.
- 16 G. E. Boyd and Q. V. Larson, *J. Am. Chem. Soc.*, 1969, **91**, 4639.
- 17 S. K. Patnaik and P. K. Mahrana, *Radiochem. Radioanal. Lett.*, 1982, **53**, 367.
- 18 W. E. Garner, *Chemistry of the Solid State* (Butterworths, London, 1955).
- 19 D. A. Young, *Decomposition of Solids*, in *The International Encyclopedia of Physical Chemistry and Chemical Physics* (Pergamon Press, Oxford, 1966).
- 20 W. B. Hannay, *Decomposition Reactions*, in *Treatise on Solid State Chemistry* (Plenum Press, New York, 1976), vol. 4.
- 21 B. V. Erofeev, *C. R. Seances Acad. Sci.*, 1946, **52**, 5111.

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