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KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION REACTIONS OF MIXED OXIDES OF SELENIUM AND TELLURIUM

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ABSTRACT

A comparative study of the thermal decomposition processes of Te_3SeO_8 and $TeSeO_4$ has been carried out based on the results obtained directly by a Mettler TA 3000 apparatus and from calculations using other differential and integral methods.

INTRODUCTION

The kinetic study of non-isothermal decomposition processes has been the subject of a considerable number of publications, probably because of its comparative experimental simplicity with respect to isothermal methods. Numerous methods have been proposed for the evaluation of the results obtained under these conditions; recently commercially available equipment (Mettler TA 3000) has incorporated in its processor software a program to calculate the kinetic parameters of the process under study.

Although in this paper neither a discussion of the significance of the kinetic results, nor the formulation of the reaction models, which would necessarily require the obtention of additional data, is attempted, the kinetic equations which best fit the reactions studied have been established with complete certainty. In this way the calculated data will have sufficient viability to be of use in later kinetic studies.

Thus it is of interest to carry out a comparative treatment of the results obtained directly from the Mettler TA 3000 apparatus with those determined by the application of other methods of kinetic analysis.

The products on which this study was carried out have been previously prepared and characterised by the authors [1]. The Freeman–Carroll method [2], together with the modification to this method proposed by one of the authors [3] and the integral method of Gorbatchev [4] modified by Šesták [5] were selected for the analysis of the

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results. These results obtained will add details to the structural models proposed for these compounds, Te_3SeO_8 and $TeSeO_4$, as has been demonstrated for related systems [6,7].

EXPERIMENTAL

The starting materials were mixed oxides of chalconide not previously described to which the formulae Te_3SeO_8 and $TeSeO_4$ were assigned.

The thermal decomposition processes studied were

$$Te_3SeO_{8(s)} \xrightarrow{420-550°C} 3\ TeO_{2(s)} + SeO_{2(g)}$$

and

$$TeSeO_{4(s)} \xrightarrow{325-415°C} TeO_{2(g)} + SeO_{2(g)}$$

The DSC curves were obtained using a Mettler TA 3000 system equipped with a TA processor TC 10 unity and DSC 20 cells.

RESULTS AND DISCUSSION

Te_3SeO_8

Figure 1 shows the DSC curve corresponding to the thermal decomposition of this product.

The kinetic parameters calculated directly by the Mettler TA 3000 equipment are given in Table 1 together with the results obtained by applying the Freeman–Carroll, integral and modified Freeman–Carroll methods.

In this case, the integral method is ambiguous in its determination of the order of the reaction. The graphs of $\ln[-\ln(1-\alpha)] - 2\,n \ln T$ against $1/T$ give straight lines, associated with coefficients of correlation near to 0.99 in all cases, for all values of n between 0.0 and 1.0, as shown in Table 2.

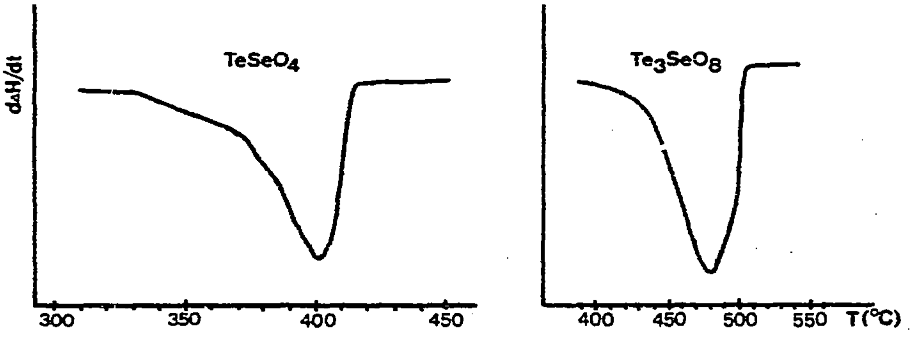

Fig. 1. DSC curves corresponding to the thermal decomposition of Te_3SeO_8 and $TeSeO_4$.

TABLE 1

Kinetic parameters obtained for the thermal decomposition process of Te_3SeO_8

Methods	Reaction order n	Activation energy E^* (kJ mole^{-1})
Mettler	0.46	252.7
Freeman–Carroll	4.01	287.5
Gorbatchev–Šesták	?	272.7
Modified Freeman–Carroll	0.93	251.1

However the dispersion observed in the corresponding values of the activation energies is relatively small (less than 2%) with respect to the average value given in Table 1. Thus, although the values calculated for the activation energies by the four methods are relatively in agreement, the values for the order of the reaction are not equally significant. If a value of $n = 1$, that determined by the modified Freeman–Carroll method, is in principle accepted as valid, the expression for the general rate equation is

$$\frac{d\alpha}{dt} = Z\,e^{-E^*/RT}(1-\alpha)$$

which, on taking logarithms becomes

$$\ln\frac{\alpha'}{(1-\alpha)} = \ln Z - \frac{E^*}{R}\,\frac{1}{T}$$

and so the plot of $\ln\,\alpha'/(1-\alpha)$ against $1/T$ will be a straight line of gradient $-E^*/R$. This plot is shown in Fig. 2; the value obtained for the activation energy,

TABLE 2

Values of n and E^* calculated by the application of the integral method for the thermal decomposition of Te_3SeO_8

n	E^* (kJ mole^{-1})	Correlation coefficient
0.1	272.7	0.987
0.2	271.6	0.987
0.3	270.3	0.987
0.4	269.1	0.987
0.5	267.9	0.987
0.6	266.8	0.987
0.7	265.6	0.987
0.8	264.4	0.987
0.9	263.2	0.986
1.0	262.0	0.986

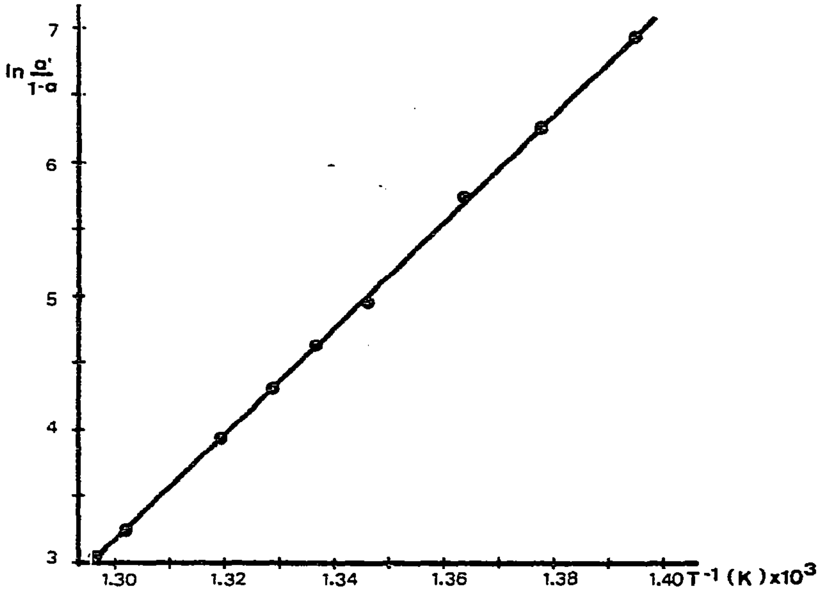

Fig. 2. Plot of $\ln \alpha'/(1-\alpha)$ against $1/T$ for Te_3SeO_8.

using the least squares method to define the best line is $E^* = 250.0$ kJ mole^{-1}, with a coefficient of correlation of 0.9993.

From all these results it is concluded that the best value for the order of the reaction is $n = 1$. For any other value of n considered the plots obtained depart progressively from linearity as the value of n departs from unity.

$TeSeO_4$

The DSC curve corresponding to the thermal decomposition of this material is shown in Fig. 1.

The kinetic parameters obtained directly by the Mettler TA 3000 equipment are given in Table 3 together with those deduced by the application of the Freeman–Carroll and modified Freeman–Carroll methods. Analogous to that registered for

TABLE 3

Kinetic parameters for the thermal decomposition process of $TeSeO_4$

Methods	Reaction order n	Activation energy E^* (kJ mole^{-1})
Mettler	0.37	202.5
Freeman–Carroll	0.26	146.5
Gorbatchev–Šesták	?	261.1
Modified Freeman–Carroll	0.04	145.5

TABLE 4

Values of n and E^* calculated by the application of the integral method for the thermal decomposition of $TeSeO_4$

n	E^* (kJ mole^{-1})	Correlation coefficient
0.1	261.1	0.993
0.2	260.8	0.993
0.3	258.9	0.993
0.4	257.8	0.993
0.5	256.8	0.993
0.6	255.7	0.993
0.7	254.6	0.993
0.8	253.5	0.993
0.9	252.4	0.993
1.0	251.4	0.993

the previous compound, the integral method does not permit the calculation of a significant value for the order of the reaction as can be seen from the data given in Table 4.

In the case of the compound Te_3SeO_8 the distinct values of the activation energies obtained by the different methods showed little dispersion (less than 2%) with respect to the average value shown in Table 3; but for the compound $TeSeO_4$ the

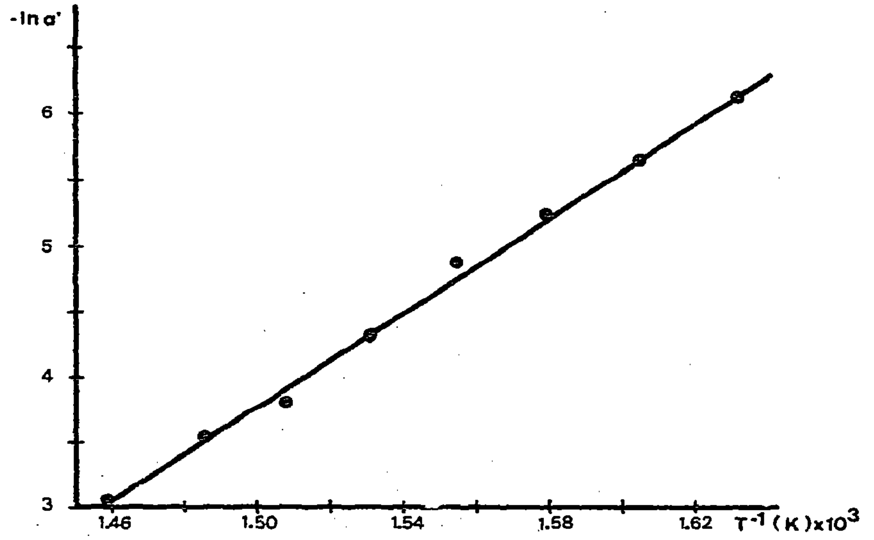

Fig. 3. Plot of ln α' against $1/T$ for $TeSeO_4$.

uncertainty in the values obtained is both for the order of the reaction and also for the energy of activation whose values vary widely. To resolve this uncertainty if, again, the value of n deduced by the modified Freeman–Carroll method is accepted as valid ($n = 0$), the expression for the rate is

$$\frac{d\alpha}{dt} = Z\, e^{-E^*/RT}$$

and taking logarithms

$$\ln \alpha' = \ln Z - \frac{E^*}{R}\frac{1}{T}$$

which indicates that the plot of $\ln \alpha'$ against $1/T$ should give a straight line of gradient $-E^*/R$.

Figure 3 shows the corresponding plot and by means of the least squares method the best fit straight line was obtained which gave an activation energy of $E^* = 146.6$ kJ mole^{-1}, associated with a coefficient of correlation of 0.9995. As with the previous compound, the plots obtained for values of the order of the reaction different from $n = 0$ were observed to depart progressively from linearity as n increased.

Without considering its possible kinetic significance which, as previously stated, was not the object of this paper, the values obtained by the application of the modified Freeman–Carroll method are those which best fit the experimental results.

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