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CONTRIBUTION TO THE FORMULATION OF A STRUCTURAL MODEL BY THE DETERMINATION OF KINETIC DATA

I. DEHYDRATION OF HEXAOXYTELLURIC ACID

C. PICO, A. JEREZ, M. L. VEIGA and E. GUTIERREZ-RIOS

Departamento de Quimica Inorgánica, Facultad de Ciencias Quimicas,
Universidad Complutense, Madrid—3, Spain

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The processes involved in the isothermal dehydration of hexaoxytelluric acid, $Te(OH)_6$, are studied and the kinetic equations and activation energies corresponding to these processes are determined. The results are in agreement with a previously proposed structural model.

This is the first of a series of papers aimed at clarifing and amplifying the details of certain imprecise structural models deduced from the results obtained by other techniques, such as X-ray diffraction, electron microscopy, infrared spectroscopy, etc.

In a previous paper [1] the conditions for the formation of the solid phases isolated in the thermal decomposition of hexaoxytelluric acid, $Te(OH)_6$, were established, which add to the results described in the literature [2—4]. This process, as regards the nature of the substances evolved, takes place in two clearly differentiated stage; the first consists of the elimination of water, and the second corresponds to the loss of oxygen to form the dioxide, paratellurite, TeO_2. During the dehydration of hexaoxytelluric acid the first stable product of definite composition which forms, in the temperature interval 130—215°, is metatelluric acid, H_2TeO_4 more correctly formulated as $TeO_3 \cdot H_2O$ [5, 6]; on increase of the temperature, the loss of water continues until complete dehydration occurs and amorphous tellurium trioxide (α-TeO_3) is obtained in the termperature interval 390—460°. Bart *et al.* have established that in an exothermic process the final phase of the dehydration overlaps the initial loss of oxygen, which thus makes it difficult to obtain accurate kinetic data. Therefore, the kinetics of the dehydration reaction have been studied by an isothermal method, in vacuum whereby it could be shown that the processes of dehydration and loss of oxygen under these condition are clearly differentiable and are not superimposed.

Experimental

The thermal decompositions were carried out in a Cahn *RG* balance with a regulated double body furnace attached to a vacuum line capable of maintaining the system at a pressure of 10^{-5} mm Hg. The sensitivity used was 2 mg per inch at a recorder speed of 2 cm per minute. The starting product was recrystallized Analar *BDH* hexaoxytelluric acid. A 50 mg sample was always used.

To study the second process of the dehydration the sample was previously maintained in vacuo (10^{-5} mm Hg) at 190° for 20 hours. Both the weight loss and the IR wpectra show the production of H_2TeO_4.

Results and discussion

Figures 1 and 2 show the rate of advance of the reaction, α, as a function of time for the processes (1) and (2):

$$Te(OH)_6 \longrightarrow H_2TeO_4 + 2\,H_2O \qquad (1)$$

$$H_2TeO_4 \longrightarrow TeO_3 + H_2O \qquad (2)$$

carried out at 270 and 300°.

The kinetic analyses undertaken were based on the method proposed by Sharp [7], which suggests kinetics of the type

$$-\ln(1-\alpha) = kt.$$

Figures 3 and 4 show $-\ln(1-\alpha)$ plotted against t for both processes was calculated from the gradients of the lines obtained by using the Arrhenius equation, which gives for reaction (1): $E^* = 8.7$ kcal/mole and for reaction (2): $E^* = 15.8$ kcal/mole. If both dehydration processes effectively correspond to a kinetic equation of the type proposed, it is evident that the equation

$$\frac{d\alpha}{dt} = k\alpha$$

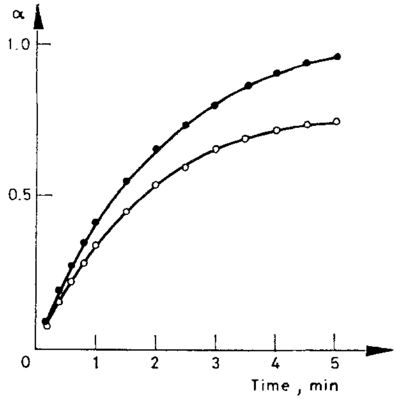

Fig. 1. Rate of avance of reaction for the process. $Te(OH)_6 \rightarrow H_2TeO_4 + 2\,H_2O$; ○ 270°; • 300°

must be obeyed; accordingly, the graph of dα/dt against α must give a straight line from whose gradient it will be possible, as before, to obtain the corresponding activation energies.

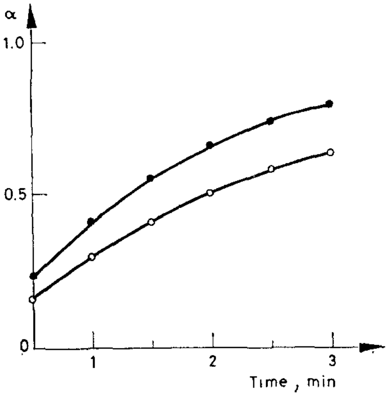

Fig. 2. Rate of avance of reaction for the process. $H_2TeO_4 \rightarrow TeO_3 + H_2O$; ○ 270° • 300°

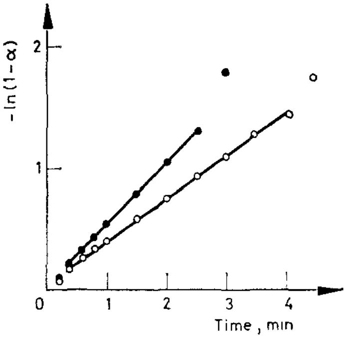

Fig. 3. $-\ln(1-\alpha)$ against t for the process, $Te(OH)_6 \rightarrow H_2TeO_4 + 2H_2O$ • 270° • 300°

The graphs of dα/dt against α are shown in Figs 5 and 6. It can be seen that the fit is good within a fairly wide interval ($\alpha = 0.2$ to 0.7). The calculation of the activation energies from the gradients of these lines gives the following results: for reaction (1) $E^* = 8.0$ kcal/mole, and for reaction (2) $E^* = 14.4$ kcal/mole.

The small temperature interval over which the dehydration reaction

$$H_2TeO_4 \longrightarrow TeO_3 + H_2O$$

takes place in vacuum (270 – 310°) introduces a component of error into the values determined. By the simultaneous use of both differential and integral methods for the analysis of the kinetic results, an attempt is made to reduce this error. The agreement between the values obtained for the activation energies by both procedures for both dehydration processes seems to indicate that the experimental method is adequate even over such a reduced temperature interval.

The kinetic equation $-\ln(1-\alpha) = kt$ obtained for the processes is normally attributed to a decomposition reaction in which the interface propagates in all directions at a constant velocity [8]. In the course of its dehydration in air, monoclinic hexaoxytelluric acid [1] loses its crystal structure, giving rise to a series of products amorphous to X-rays, until the composition TeO_3 is reached. The absence of order is thus in agreement with the model to which the kinetic equations obtained correspond.

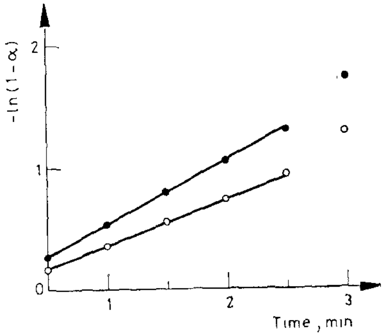

Fig. 4. — ln(1-α) against *t* for the process, $H_2TeO_4 \rightarrow TeO_3 + H_2O$; ○ 270°; • 300°

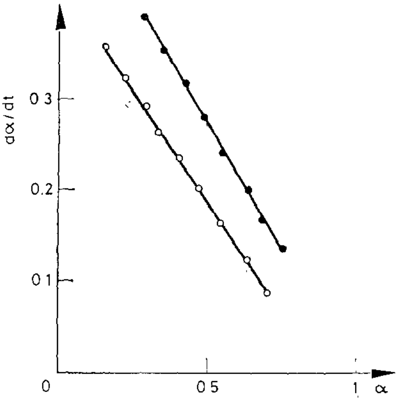

Fig. 5. dα/dt against *t* for the process. $Te(OH)_6 \rightarrow H_2TeO_4 + 2\,H_2O$. ○ 270° • 300°

In a previous paper [5] a structural model for the dehydration process was proposed, according to which the elimination of water molecules could be brought about as a consequence of an olation process between adjacent octaedral $Te(OH)_6$ groups, forming H_2TeO_4 whose structure, related to that of ReO_3, would contain water molecules in the interstices of 12-fold coordination, and the resulting product can be thought to have the formula $TeO_3 \cdot H_2O$. The structural changes following such processes allow the starting of the loss of the remaining water molecule, in such a manner that reaction (2) begins when α for reaction (1) is equal to about 0.8.

The elimination of the last water molecule gives rise to anhydrous TeO_3. The value of the activation energy determined for this process is markedly higher than that for the first process, which is in agreement with the structural model proposed.

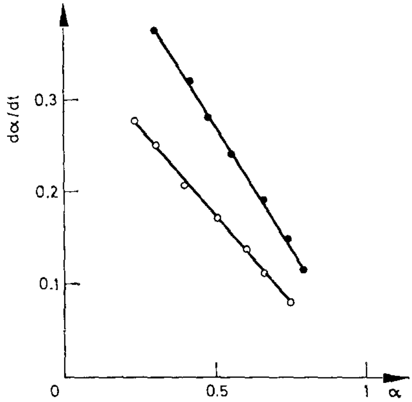

Fig. 6. $d\alpha/dt$ against t for the process. $H_2TeO_4 \rightarrow TeO_3 + H_2O$; ○ 270° ● 300°

References

1. C. Pico, M. L. Veiga and E. Gutierrez Rios, An. Quím., 73 (1977) 816.
2. J. Rosicky, J. Loub and J. Pavel, Z. Anorg. Allgem. Chem., 334 (1965) 312.
3. O. N. Breusov, O. I. Borob'eva, N. A. Druz', T. V. Revzina and B. P. Sobоliev, Izvest. Akad. Nauk. S. S. S. R. Neorg. Materialy, 2 (1966) 308.
4. J. C. J. Bart, A. Bossi, P. Perissinoto, A. Castellan and N. Giordano, J. Thermal Anal., 8 (1975) 313.
5. C. Pico, E. Gutierrez Puebla and E. Gutierrez Rios, An. Quím., 73 (1977) 951.
6. H. Siebert, Z. Anorg. Allgem. Chem., 301 (1959) 161.
7. E. Sharp, J. Amer. Ceram. Soc., 8 (1963) 374.
8. D. A. Joung, Decomposition of Solids, Pergamon, 1966, p. 32.

Résumé — On a étudié les réactions qui interviennent lors de la déshydratation isotherme de l'acide hexaoxytellurique $Te(OH)_6$ et déterminé les équations cinétiques ainsi que les énergies d'activation correspondantes. Les résultats sont en accord avec un modèle structural proposé préalablement.

Zusammenfassung — Die an der isothermen Dehydratisierung der Hexaoxytellursäure $Te(OH)_6$ beteiligten Vorgänge wurden untersucht und die diesen Vorgängen entsprechenden kinetischen Gleichungen und Aktivierungsenergien bestimmt. Die Ergebnisse sind mit einem früher vorgeschlagenen strukturellen Modell in Übereinstimmung.

Резюме — Изучены процессы изотермической дегидратации гексаоксителлуровой кислоты, $Te(OH)_6$, б определены кинетические уравнения и энергии активаций соответствующих процессов. Результаты согласуются с ранее предложенной структурной моделью.