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THE THERMAL DEHYDRATION OF $Sr(HCOO)_2 \cdot 2(H, D)_2O$. INFLUENCE OF THE ISOTOPIC SUBSTITUTION ON THE KINETICS

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The kinetics of thermal dehydration of $Sr(HCOO)_2 \cdot 2(H, D)_2O$ were investigated using a dynamic thermogravimetric technique. Differences were found when the hydrogen was partially substituted by deuterium. These differences were explained by means of a microscopic approach based on the static and dynamic microscopic properties.

The present work deals with an investigation of the kinetics of thermal dehydration of $Sr(HCOO)_2 \cdot 2H_2O$ (strontium formate dihydrate, SFDH) with different extents of isotopic substitution H_2O/D_2O of its crystallographic water. Previous work on SFDH dehydration [1–3] and on the anhydrous salt [4] has been carried out in our laboratory.

It is well known that the determination of kinetic parameters from thermal analysis presents some difficulties, mainly because of certain experimental parameters such as heating rate, sample mass, etc. A tool to perform such a kinetic study is the total or partial substitution of proton-containing water by deuterium-containing water.

In this paper, the TG technique has been used as the main experimental procedure to examine the kinetics and thermodynamics of the dehydration of SFDH. Simultaneously, DTA curves were recorded, and DSC data published elsewhere [2] were used to compare with the actual TG data. It should be pointed out that the DSC results do not account correctly for the mass loss.

The kinetic information obtained from this macroscopic process has been related with the microscopic structural properties, either static or dynamic, obtained from X-ray diffraction [5] and Raman spectroscopy [6–8], respectively.

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SFDH has an orthorhombic crystal, with four asymmetric molecules in the unit cell (Fig. 1) [5]. The water molecules are situated in two non-equivalent general positions W(1) and W(2) in [2–6].

The W(1) water molecules are tetrahedrally coordinated, with the lone pairs bonded to two strontium ions (distances Sr–O: 2.649 Å and 2.674 Å), the hydrogen participating in two markedly different hydrogen-bonds. One is directed to the formate oxygen O(4), with an 0...0 distance of 2.672 Å, and the other to the water molecule W(2), with an 0...0 distance of 2.808 Å. One of the lone paires of the W(2) water molecules is bonded to the strontium ion with the Sr–O distance equal to 2.640 Å, and the other one acts as the acceptor of the hydrogen atom of the W(1) molecule in a hydrogen-bond with a length of 2.808 Å, as mentioned above. The hydrogen atoms of the W(2) water molecules participate in hydrogen-bonds with oxygens O(2) and O(4) of the formate ions. The distances are 2.736 Å and 2.715 Å, respectively.

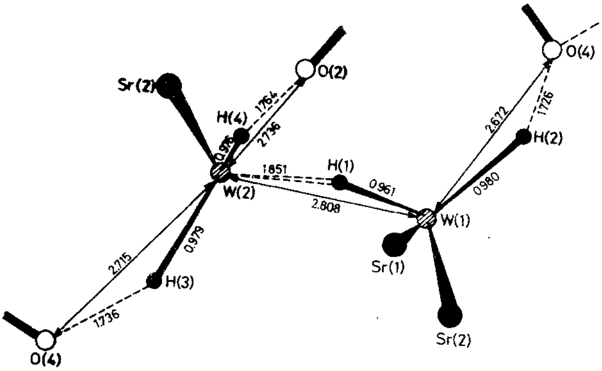

Fig. 1 Structure environment of the water molecules in the strontium formate dihydrate crystal (Distances in A)

Experimental

Strontium formate dihydrate was prepared by the reaction of strontium carbonate and formic acid, at 50° in order to facilitate the decomposition of the carbonate, and was recrystallized twice from water [9]. The material was air-dried and used as the solute in saturated growth solutions.

Isomorphic crystals of $Sr(HCOO)_2 \cdot 2(H, D)_2O$ were obtained by dehydrating SFDH under vacuum at 105°, followed by its dissolution in 99.99% pure D_2O or D_2O/H_2O mixtures, and thereafter growing in a similar manner as for the hydrated salt.

We shall use the numbers 1, 2, 3, 4 and 5, respectively, to refer to the crystals with

Table 1 Correlation factors of the crystals 1 to 5, assuming the function $f(\alpha) = (1-\alpha)^n$ and a single stage process

Crystal	Reaction order	Correlation factor
SFDH 1	1.9	0.98691
SFD(H/D)2	1.7	0.98619
SFD(H/D)3	1.9	0.98528
SFD(H/D)4	1.8	0.98555
SFDD 5	1.9	0.98824

100%, 80%, 56%, 31% and 2% of H_2O. These percentages were measured from the stretching Raman band ratio $\nu(OH)/\nu(OD)$ for each crystal [2] and verified by calculations from the mass loss curves.

A Stanton Redcroft 180 apparatus was used for the thermogravimetric analysis. The experiments were carried out at a fixed heating rate (ca. 3 deg $\min^{-1}$), under a N_2 stream (50 ml $\min^{-1}$), using an open crucible and no more than 10 mg of crystal sample, carefully ground with a pestle and mortar. The Stanton Redcroft design meant that we were able to run the DTA simultaneously. The temperature range for the dehydration process was from 46° to 79°.

Analytical method

The process of loss of water may be understood well through a knowledge of the kinetic parameters of the reaction. It is accepted that the reaction proceeds in accordance with the well-known expression

$$\frac{d\alpha}{dT} = \frac{Z}{\beta}\exp(-E/RT)f(\alpha) \tag{1}$$

where α is the fraction of solid reactant decomposed at time t, the temperature T is linearly related to the time t by the heating rate β, and Z and E are the kinetic parameters, i.e. the preexponential factor and the activation energy. The functions $f(\alpha)$ were initially considered from the work of Šesták and Berggren [10]. These kinetic functions are based on the geometrical description of heterogeneous processes, regardless of the physical hypothesis.

The kinetic parameters and the optimum kinetic function $f(\alpha)$ were obtained by solving Eq. (1). We shall use the integral method described by Šatava [11], which is based on the solution of

$$\ln g(\alpha) - \ln p(E/RT) = \ln\frac{ZE}{R\beta} \tag{2}$$

with

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)}$$

and

$$p(x) = \int x^{-2} \exp(-x)\,dx \qquad x = E/RT$$

To find the adequate kinetic function $g(\alpha)$ from Eq. (2), it must be considered that $\ln p(x)$ depends linearly on T^{-1} for high values of x, which is the case. Therefore, if the r.h.s. of Eq. (2) is independent of temperature, the correct function of $g(\alpha)$ will be that whose logarithm gives the best fit to a straight line *vs* $1/T$. In this way, we tried to fit our experimental curves, with the result that none of the kinetic functions $g(\alpha)$ given in [10] were good enough. The linear regression factors were of order 0.9 or lower. Moreover, we understand that in general the reaction is unlikely to proceed exactly as predicted by the functions used, which correspond to an idealized model and are based exclusively on geometrical criteria.

Consequently, we shall adopt another function, described by

$$f(\alpha) = (1-\alpha)^n$$

where n can be any positive number, referred to as the kinetic "order". Firstly, this function has been taken because of the tendency observed in the previous calculation, where the best fit was found with the kinetic functions $(1-\alpha)$ and $(1-\alpha)^2$. Secondly, the proposed function provides reliable and statistically objective values of the kinetic parameters, as we can conclude from the coherence of the results presented here.

Another argument can be used to explain this assumption, based on the meaning of the expressions $(1-\alpha)$, $(1-\alpha)^{1/2}$ and $(1-\alpha)^{1/3}$. The first equation is that of first-order random nucleation, which means that the reaction ratio is governed exclusively by the bond breaking. If the control of the reaction velocity is taken by the expansion (or growing) of this bond breaking, the kinetic function is $(1-\alpha)^{1/2}$ (cylindrical growth) or $(1-\alpha)^{1/3}$ (spherical growth). This phase-boundary growth means, in some way, that an interaction can take place between the molecules which are being broken. This implies that the power of $(1-\alpha)$ can be different from 1/2 or 1/3, being greater than one if the interaction is strong enough. A similar treatment in a different phenomenon (TSDC) allows verification of the former conception, once the use of the $(1-\alpha)^n$ expression has been accepted [12].

Results and discussion

Figure 2 gives thermogravimetric curves for the crystals previously described. For the crystals containing some amount of D_2O, these curves are similar to the mass loss curve for SFDH crystals (number 1, not deuterated). The results obtained from the analytical method described previously are not good enough, assuming that the dehydration process involves a single stage.

The fact that the water molecules occupy two different crystallographic positions and the presence of a shoulder in the DTA curve of the dihydrate crystal (SFDH, crystal number 1), as shown in Fig. 3, suggest the existence of two activation energies. The structural data [5] indicate that these energies are not necessarily very different, but in the record of the mass loss some differences can be found. In consequence, we propose to study the kinetic curve as a single stage, but with two parts, i.e. with two different "orders" in the kinetic function $(1-\alpha)^n$. In this way, the fitting of the kinetic equation (1) gives excellent correlation factors for this type of kinetic process. The values of the reaction order, the activation energies, the preexponential factors and the correlation factors for the five crystals are collected in Table 2. The division into two parts has been done using the maximum points of the DTA curves as reference, corresponding approximately to $\alpha = 0.65$.

It is important to observe that the kinetic parameters of the two parts are substantially different, but that if the process were to proceed continuously, without differentiation into two parts, the kinetic parameters obtained with the assumption

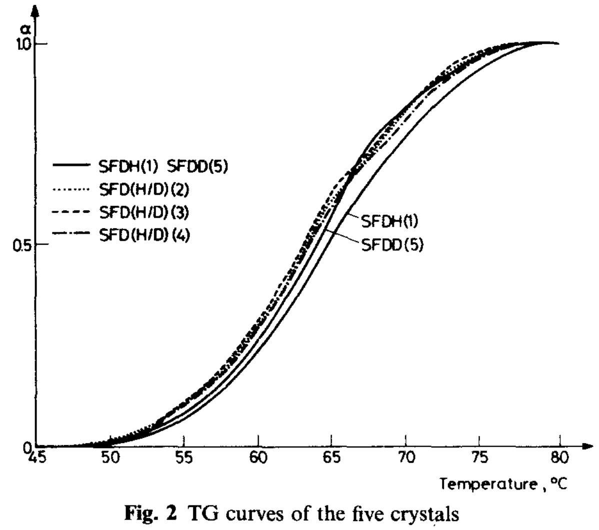

Fig. 2 TG curves of the five crystals

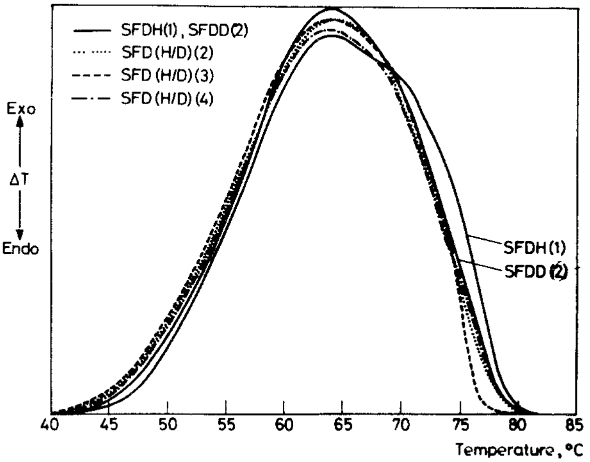

Fig. 3 DTA curves of the five crystals

Table 2 Kinetic parameters of the crystals 1 to 5 with two parts process

Crystal	1st part				2nd part			
	n	E, kJ mol^{-1}	Z, s^{-1}	r	n	E, kJ mol^{-1}	Z, s^{-1}	r
SFDH 1	3.5	296	1.63 E44	0.99897	0.75	89.4	2.45 E11	0.99886
SFD(H/D)2	3.1	273	3.94 E39	0.99792	0.85	105.6	1.14 E14	0.99984
SFD(H/D)3	2.9	285	4.47 E42	0.99749	0.70	99.8	8.18 E11	0.99679
SFD(H/D)4	2.8	266	4.05 E39	0.99898	0.75	90.8	4.28 E11	0.99794
SFDD 5	2.2	264	1.70 E39	0.99693	0.55	57.1	2.08 E06	0.99927

of two parts should be very similar. It is clear that this is not the fact and this therefore justifies acceptance of the hypothesis concerning two parts.

From our results it seems reasonable to relate the macroscopic fact of mass loss to the static and dynamic microscopic properties. The X-ray diffraction results have shown that the two water molecule families are bonded to the Sr^{2+} ions through the oxygen atoms, with comparable bond lengths. The valence contributions of the strontium to the oxygens of the water, and hence the energies, are very similar for the two families. These bonds are therefore not responsible for the kinetic differences found for our crystals, in spite of their contribution to the dehydration process. Consequently, the secondary or less energetic bonds are responsible for the differences in the dehydration curves.

This latter argument was supported by the general assumption that the weak hydrogen-bonds of the crystals play an important role in the physical-chemistry properties, and mainly in their variation with the temperature [2, 8].

An important parameter which must be considered in the study of the process of mass loss is the activation energy. From the correlation of the degree of deuteration and the activation energy (Table 2), it can be deduced that the energy given to the sample decreases as the concentration of D_2O increases. Nevertheless, in the crystals with partial isotopic substitutions some particularities exist in the activation energy; these can be explained in terms of the microscopic development of our compounds.

From the structural environments of the two water molecules, W(1) and W(2), shown in Fig. 1, it may be seen that W(1) has two hydrogen-bonds with clearly different bond lengths. This implies that its vibrations are decoupled [7]; consequently, W(1) will be more unstable as concerns thermal excitation than W(2), which bonds through its hydrogen with the other oxygen atoms, with similar bond lengths.

Savatinova et al. [13] have recently pointed out that, depending on the initial ratio of H_2O/D_2O in the solution, the chemical species HOD can be present in appreciable amount. This species will also play an important role in the crystals obtained from the solutions of H_2O/D_2O [14]. The HOD molecule has an asymmetric character, and it will therefore preferentially occupy the most asymmetric site, i.e. the W(1) site, and it will establish deuterium-bonds between the two water molecules W(1)...D...W(2) [7]. Raman spectroscopy was used [2, 7, 8] to determine the presence of HOD in a specific crystallographic position. This bond and the two hydrogen-bonds of the W(2) molecule seem to be responsible for the first part of the dehydration process. The strongest bond (2.672 Å), which involves W(2), shows a relevant role in the second part of the dehydration process.

The differences in the energies of the processes arise from the crystallographic differences caused by the degree of deuteration. Crystals 2 and 4 must have less energy in the first part of the process than that of the homologous SFDH 1, since this part is conditioned by the presence of deuterium in the weaker hydrogen-bond. On the other hand, the energies of these two crystals in the second part will be similar, because of the large amount of hydrogen involved in the strongest bond (W(1)...O(4)).

For crystal number 3, the three molecular groups H_2O, D_2O and HOD make similar contributions to the constitution of the crystal [13, 14]. Thus, its configuration is energetically more consistent with those of crystals SFDH 1 (totally hydrogenated) and SFDD 5 (almost totally deuterated). Furthermore, its temperature interval is a few degrees lower than in the other records, which confirms that these three groups coexist in the crystal, making its structure not totally ordered and therefore easier to excite thermally.

Crystal FSDH 5 has lower energies in both parts of the kinetic curve, due to the fact that almost all bonds are of O...D type and only very few are of O...H type.

In conclusion, the process of dehydration of strontium formate with two molecules of water and its homologues with partial substitution of H_2O by D_2O is regulated mainly by the breaking of the bonds, which constitutes the generation of nuclei at random, the transport stage being irrelevant in the kinetic process (fast diffusion). The differences obtained in the kinetic process are due to the different energetic environments of the W(1) and W(2) sites in the general structure.

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References

1 A. C. Prieto, A. González, E. Hernández, F. F. Rull and J. A. de Saja, Crystal Res. & Technol., 18 (1983) 1093.
2 A. C. Prieto, Ph. D. Thesis, University of Valladolid, Spain, 1984.
3 F. Martin, Tesis de Licenciatura, University of Valladolid, Spain, 1983.
4 A. González, J. Jiménez and F. Rull, Crystal Res. & Technol., 20 (1985) K11.
5 J. L. Galigné, Acta Cryst., B27 (1971) 2469.
6 A. C. Prieto, F. Rull and J. A. de Saja, Boletin de la Sociedad Española de Mineralogía (1986) in press.
7 A. C. Prieto, F. Rull and J. A. de Saja, J. Mol. Structure, 143 (1986) 117; J. Mol. Structure in press.
8 A. C. Prieto, F. Rull and J. A. de Saja, Proceedings of the II Simposio Ibérico de Física de la Materia Condensada, Sevilla, p1-7 (1986) 69.
9 R. Vierne, DES, University of Montpellier, France, 1957.
10 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
11 V. Šatava, Thermochim. Acta, 2 (1971) 423.
12 a) A. Torres, J. Jiménez, J. C. Merino, J. A. de Saja and F. Sobron, J. Phys. Chem. Solids, 46 (6) (1985) 665; b) A. Torres, J. Jiménez, B. Vega and J. A. de Saja, Phys. Stat. sol., 90 (1985) 749.
13 I. Savatinova, E. Anachkova and R. Nikolaeva, Spectrosc. Lett., 19(2) (1986) 167.
14 H. D. Lutz, J. Henning, W. Buchmeier and B. Engelen, J. Raman Spectrosc., 15 (1984) 423.

Zusammenfassung — Die Kinetik der thermischen Dehydratisierung von $Sr(HCOO)_2 \cdot 2(H, D)_2O$ wurde mittels dynamischer Thermogravimetrie untersucht. Bei partieller Substitution von Wasserstoff durch Deuterium wurden Unterschiede gefunden, die durch eine auf den statischen und dynamischen mikroskopischen Eigenschaften beruhende Betrachtungsweise erklärt werden.

Резюме — Методом динамической ТГ исследована кинетика термической дегидратации $Sr(HCOO)_2 \cdot 2(H, D)_2O$. При частичном замещении водорода на дейтерий обнаружены определенные различия, которые объяснены на основе статических и динамических микроскопических свойств.