SIGNIFICANCE OF STRUCTURAL FACTORS
IN THE THERMAL DISSOCIATION OF SOLIDS

L. STOCH

Academy of Mining and Metallurgy, 30-059 Kraków (Poland)

ABSTRACT

The usefulness of traditional methods for describing the kinetics of the thermal decomposition of solids is limited to substances of simple structure and simple chemical composition. The development of a modern concept of the thermal dissociation of solids taking into account the specificity of their structure is an important task for thermal investigations in the near future. The mutual relationship between the parent substance and the solid decomposition products as the main factor characterizing the decomposition of solids is proposed. These relationships for topochemical and intracrystalline thermal dissociation processes are discussed.

INTRODUCTION

The development of thermal analysis methods resulted in considerable progress in investigations of the thermal dissociation of solids. However, investigations of dissociation are frequently limited to the formal mathematical description of the course of the process as a function of the degree of decomposition vs. time and/or the determination of the kinetic parameters (activation energy, pre-exponential factor and order of reaction). New mathematical methods of converting DTA and TG curves into mathematical equations of the hypothetical rate of the reaction are constantly being proposed.

Papers on thermal analysis contain many kinetic data on the thermal decomposition of different compounds. However, a comparison of these data and a search for more general relationships governing the thermal stability and decomposition of solids even of the same chemical type are difficult. It is a consequence of the specific structure of solids, distinguishing them from liquids and gaseous substances and the anisotropic properties of solids, owing to their rigid framework.

As a result, the kinetic constants of the thermal dissociation of solids are actually functions of variables that are difficult to establish and the physical

meaning of which is not clear. The development of modern concepts of thermal dissociation of solids is an important task in thermal investigations for the near future. In this concept the effect of structural factors should be taken into consideration. This problem may be solved by different methods, and one of the possible approaches that may be suggested on the basis of the results of some recent investigations is presented below.

A factor differentiating the processes of thermal dissociation of solids may be the mutual relationship between the parent substance and the solid decomposition product which is being formed [1]. This relationship depends on, among other things, the nature of the bonds and the structure of the substances undergoing dissociation. It is a consequence of the decisive role of structural factors in the course of these processes.

Pressure of the gaseous products of decomposition is another factor that influences the course of the thermal dissociation of solids and its kinetics.

MUTUAL RELATIONSHIP BETWEEN PARENT SUBSTANCE AND SOLID PRODUCTS OF DISSOCIATION

On the basis of the available data concerning mutual relationships between the parent substance and the solid products of the decomposition of a number of inorganic compounds and minerals, the processes of thermal dissociation can be divided into two groups: topochemical thermal dissociation; and intracrystal thermal dissociation.

We can distinguish several types of reactions of topochemical and intracrystal thermal dissociation (Table 1). As the topochemical reaction we shall consider the heterogenic reaction that occurs on the surface of a substance being a substrate. The rate of this reaction is limited by the rate of chemical interaction in the reaction centre or by the diffusion of the gaseous product through the layer of the solid dissociation products. The thermal dissociation usually proceeds together with the formation of a layer of solid products around the grain of the parent substance (dissociation of carbonates and sulphates, dehydration of hydrates, etc.).

In solid bodies, one can observe reactions occurring in the whole volume of the crystal grain and consisting in the displacement of electrons or atoms. First, a change in the colour of the substance may take place. Second, rearrangement of the structure or a change in the degree of the crystal lattice order occurs. These changes occur inside the structural framework, sometimes without changing the outward form of the solid body. Some of them may be the result of heating the substance and may lead to thermal dissociation (oxidation of divalent iron in vermiculite, accompanied by elimination of OH groups).

These reactions differ from those taking place in liquids in that they proceed in the area of the influence of the crystal field and the displacement

TABLE 1

Characteristic types of thermal dissociation processes

No.	Localization of reaction centres	Governing factor [a]
Topochemical dissociation		
A-1	Dissociation at the surface of the parent solid substance–gaseous products boundary. Process leading to the complete decomposition of substance, no solid products are formed. Decomposition of ammonium salts is an example.	p_{gp} in air
B-1	Dissociation at the parent substance–solid product phase boundary. Product form an outer layer, separated from parent substance with distinguishing boundary. Process runs according the model of contracting sphere or disc (simple carbonates, sulphates, some hydrates, etc.).	p_{gp} at boundary
B-2	Dissociation at the parent substance–solid product boundary, accompanied by recombination of gaseous products and synthesis of new compounds stable at the temperature of dissociation (decomposition of complex carbonates, dehydration of some hydrates, etc.).	p_{gp} in product layer
Intracrystal dissociation		
C-1	Intracrystal dissociation—decomposition centres are distributed within the whole volume of the crystal of the parent substance. Grains of the product are growing within the crystal of the parent substance and remain in topotactic relation with it [$Ca(OH)_2$, $Mg(OH)_2$ etc.].	Intracrystalline pressure in domains
C-2	Intracrystal dissociation—decomposition centres are distributed within the whole volume of the crystal of the parent substance. After the dissociation the essential framework of its structure remains preserved or a new solid phase is formed inside the crystal by the transformation of the structure of the parent substance (layer silicates, hemimorphite, some hydrates).	Intracrystalline pressure in domains

[a] p_{gp} = partial pressure of gaseous product.

of the electrons and atoms are directional, the directions being dependent on the internal structure of the solid body. Here the diffusional displacements are considerably slower than in liquids.

Thermal dissociations of this type include the removal of the structural OH groups, i.e., dehydroxylation of hydroxides and layer silicates [2]. During this process the centres of the dissociation are located more or less uniformly inside the crystal grain of the hydroxide undergoing dissociation,

and the water vapour molecules are forming also in its entire volume. The solid product of the reaction is formed inside the parent substance and its structure remains in topotactic relation with respect to the original structure of the hydroxide [3]. The thermal dissociation of layer silicates has a similar character.

Considering the location of the dissociation centres and the fact that the new phase develops inside the crystal of the parent substance without forming a separate external layer of the products, the term "intracrystal dissociation" is proposed for this type of dissociation [2].

Dehydroxylation of layer silicates represents a peculiar type of intracrystal thermal dissociation (Table 1). Dehydroxylation of kaolinite is one of the best known processes of this kind [4].

Such a course of thermal dissociation is due to the exceptionally distinct anisotropy of the distribution of the strengths of bonds in layer silicates. The anisotropy of the kaolinite structure is expressed by (1) strong ionic–atomic silicon–oxygen and alumina–oxygen bonds within the layer and (2) weaker hydrogen bonds between layers. In metakaolinite, a dehydrated form of kaolinite, the original structure is preserved in the plane of the a and b axes but is lost in the third (c) direction.

We may assume that owing to the intracrystalline character of dehydroxylation, its kinetics are determined by the partial pressure of water in definite volumes of the crystal structure—intracrystalline pressure. These volumes may be defined as thermochemical domains, by analogy with the term "domain" used for the minimal part of the crystal structure coherently diffracting X-radiation. Thermochemical domains are spaces free from structural discontinuities, bordered by dislocations, boundaries of mosaic blocks and other defects together with which gaseous products of reaction can escape. The thermal dissociation process starts when the intracrystalline pressure within domains exceeds the value necessary to disrupt the weakest chemical bonds.

The size of the domains depends on structural imperfections and the crystal size and determines the critical value of the intracrystalline pressure. It explains the well known relation between the degree of crystallinity and the shape of DTA curves of kaolinite polytypes [2,4].

Recent investigations of the dehydration of syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$, revealed that the habit of its crystals is preserved during the process. Syngenite has a layer structure with channels that allow water molecules to leave. The structures of the parent substance and the anhydrous product have a topotactic relationship [5]. The process seems to be intracrystal dissociation (Table 1, C-2).

Serra et al. studied the dehydration of aquoammine-metal(III) salts [6]. They found that the packing ability of the ions (free space) seems to be a determining factor of the process. The greater the free space capacity, the lower is likelihood of water molecules leaving the lattice and the greater is

the activation energy. This finding corresponds to the concept of the intracrystalline pressure in thermochemical domains.

Localization of topochemical reactions was studied systematically by Prodan [7,8]. He indicated that the arrangement of the decomposition centres on the crystal surface is not uniform. The centres appear first on some faces, spreading out in their plane and forming decomposition spots. As a result, the dissociation develops at various rates in different crystallographic directions. The study of these phenomena enable the effects of the morphology of the crystals and their size on the kinetics of thermal dissociation to be ascertained. This constitutes important progress in investigations of the thermal dissociation of solids as a development and extension of the earlier studies by Delmon [9].

Localization of decomposition reactions may change. Depending on the temperature and water vapour pressure, disproportionation of Mn phosphates is localized on the surface or inside the crystal [8].

The spot surface localization of topochemical reactions makes the kinetic model more complicated. In addition to taking into account the fact that crystal faces react non-simultaneously, it is also necessary to consider the nature of active centres (usually of dislocation nature) and their distribution on faces, the form of the reaction surface spots and the relative velocities of their growth in different directions [7].

INFLUENCE OF GASEOUS PRODUCTS OF DECOMPOSITION

The kinetics of topochemical thermal dissociation reactions is strongly dependent on the partial pressure of the gaseous product of decomposition. It is clearly visible as a shift of the DTA peak temperature with increase in the amount of decomposing substance. This phenomenon may be used in DTA work to distinguish dissociation reactions from phase transformations [10]. Curves of peak temperature versus log (amount of sample) are helpful in the identification of minerals [11].

The partial pressure of the gaseous products of decomposition at the phase boundary limits the rate of topochemical thermal dissociation of many substances (Table 1). Its value is regulated by the rate of migration of gas through the layer of the solid product.

Early work on thermal dissociation demonstrated the influence of the partial pressure of gaseous products on activation energy of reversible thermal dissociation processes and suggested that it is a consequence of chemical interactions between solid and gaseous products of decomposition [12].

Maciejewski and Bałdyga [13] showed a greater dependence of the CO_2 pressure on the observed rate of $CaCO_3$ decomposition compared with the equations based on the Freundlich or Langmuir theories of adsorption. It is

a consequence of the chemisorption of CO_2 on the forming active CaO, which has an unstable structure intermediate between the structures of $CaCO_3$ and stable cubic CaO. The activation energy of $CaCO_3$ decomposition is a linear function of CO_2 partial pressure.

All of this suggests that in the decomposition of some substances, the reverse reaction, i.e., synthesis, runs in parallel and influences the decomposition process. Reactions in which reversibility is considerable are, e.g., the decomposition of $CaCO_3$, $SrCO_3$ and $BaCO_3$. With $MgCO_3$ reversibility occurs to a smaller extent and the dissociations of $FeCO_3$ and $ZnCO_3$ are almost irreversible. Reversibility of the reaction is understood here in the kinetic sense as the ratio of the decomposition rate to the rate of the reverse reaction, i.e., synthesis at the given temperature.

It is usually assumed that the rate of the reversible reaction is determined by the chemical affinity of the solid product for the gaseous product, which depends on the force of chemical binding [14]. The other factor determining the reversibility is the similarity between the structure of the parent substance and that of the solid product. Another factor that should be taken into consideration is the disordered state of the structure of the early solid product and the rate of its recrystallization into a stable ordered structure.

Dissociation of many substances is accompanied by recombination of the gaseous product into a solid product and a synthesis of a new, simpler compound stable at the temperature of dissociation. Minerals such as cerusite, huntite and hydromagnesite are examples. The decomposition of lead trioxynitrates [15] also seems to belong to this process.

The formation of new intermediate compounds depends on the partial pressure of gaseous products within the layer of the solid product and their reactivity. The pressure is influenced by the rate of removal of gas from the sample bed, which is determined by the experimental conditions. As a result, one can distinguish different stages of the decomposition of the same substance. Decomposition of basic ammonium and aluminium sulphates are examples [16,17].

In contrast to the decomposition of carbonates, the pressure of gaseous products only slightly influences the kinetics of the intracrystal dehydroxylation of layer silicates. As the intracrystalline pressure is very high, the changes in the partial pressure of water vapour in the environment only slightly influence the decomposition kinetics and temperature. Removal of water molecules from the interior of large perfect crystals is particularly difficult. When the intracrystalline pressure exceeds a critical value, a violent separation of the layers and a rapid increase in the volume of the sample occur (dickite, vermiculite, micas, etc.). Dehydroxylation of colemanite, $Ca(B_4O_4)OH_3 \cdot H_2O$, is also accompanied by an explosive increase in the volume of the sample.

CONCLUSIONS

Many experimental data obtained so far confirm that the thermal dissociation of solids is a structurally sensitive process. The kinetics of thermal dissociation read from thermal analysis curves may thus become a source of information of the details of the internal structure of a substance, imperfections of its structure, etc. The development of a modern concept of the thermal dissociation of solids, taking into account structural factors, is an important task for thermal investigations in the near future.

REFERENCES

1 L. Stoch, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 97.
2 L. Stoch, J. Therm. Anal., 29 (1984) 919.
3 H.F.W. Taylor, Clay Miner. Bull., 5 (1962) 45.
4 L. Stoch and I. Wacławska, J. Therm. Anal., 20 (1981) 291, 305.
5 K. Wieczorek-Ciurowa, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 485.
6 M. Serra, A. Escuer, M. Monfort and J. Ribas, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 493.
7 E.A. Prodan, J. Therm. Anal., 29 (1984) 941.
8 E.A. Prodan, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 169.
9 B. Delmon, Introduction à la Cinétique Hétérogéne, Technik, Paris, 1969.
10 L. Stoch, Arch. Mineral. (in Polish), 21 (1957) 185.
11 W. Smykatz-Kloss, J. Therm. Anal., 23 (1982) 15.
12 J. Zawadzki and S. Bretsznajder, Z. Phys. Chem., Abt. B, 22 (1933) 79.
13 M. Maciejewski and J. Bałdyga, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 105.
14 D.M. Goldin and G.V. Kulikova, J. Therm. Anal., 29 (1984) 139.
15 M.E. Garcia-Clavel, M.J. Martinez-Lope, M.T. Casais-Alvarez and A. Kilany, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 547.
16 T. Nagaishi, S. Ishiyama, J. Yoshimira, M. Matsumoto and S. Yoshinaga, J. Therm. Anal., 23 (1982) 201.
17 J. Pysiak and B. Pacewska, J. Therm. Anal., 19 (1980) 79.