Thermochimica Acta, 72 (1984) 139—146
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

EXPERIMENTAL DETERMINATION OF SPECIFIC REACTION RATES FOR SOLID STATE DECOMPOSITION PROCESSES EXHIBITING A 'CONTRACTING VOLUME' BEHAVIOUR

H.R. Oswald, A. Reller and M. Maciejewski*

Institute for Inorganic Chemistry, University of Zürich
Winterthurerstr. 190, 8057 Zürich (Switzerland)

ABSTRACT

Combined evaluation of quantitative thermoanalytical, structural and morphological investigations revealed a 'contracting volume' behaviour for the thermal decomposition of various solid metal complexes and - under high vacuum conditions - of calcite single crystals. It is shown that the determination of specific and reproducible kinetic data is not feasible unless reaction rates are defined with respect to the crystal structure and/or morphology of the initial phase. Moreover, the actual reaction mechanism is strongly dependent on the experimental conditions.

INTRODUCTION

As it has been observed by morphological and structural investigations as well as quantitative thermoanalytical measurements the course of the thermal decomposition of systems such as hydrates (ref.1), metal complexes (ref.2) and - under selected experimental conditions - carbonates (ref.3) can be described by a 'contracting volume' behaviour. For the determination of kinetic data of such processes the mathematical evaluation of time- or temperature-dependent quantitative thermogravimetric measurements of the overall weight loss cannot yield unambiguous results, since the influence of the shape of the initial material (see e.g. ref.4), different direction-dependent velocities of the initial material/product phase boundary advancements into the bulk (see e.g. refs. 2,5) as well as influences of diffusion phenomena have to be taken into account.

Together with the knowledge of the structural and compositional reaction mechanism, the measurement of phase boundary movements

---

*Present address: Institute of General and Inorganic Chemistry, Technical University, ul.Noakowskiego 3, 00-664 Warsaw (Poland)

0040-6031/84/$03.00

along given crystallographic directions determined by X-rays or - more generally - along selected coordinates as function of time, temperature or even further experimental parameters, however, leads to specific and reproducible rate constants.

THEORY

For the case of phase boundary reaction controlled decompositions exhibiting a 'contracting volume' behaviour the over-all conversion rate $\alpha = \frac{w_o - w_t}{w_o - w_\infty}$ (w_o: initial weight; w_t: actual weight; w_∞ : weight of the solid product at the end of the reaction) can be expressed in terms of the velocity of the phase-boundary advancement into the bulk as follows (see also refs.4,6).

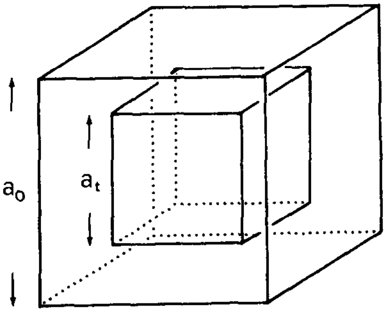

Fig. 1. Schematic representation of two stages during the thermal decomposition of a single-crystalline compound exhibiting a 'contracting volume' behaviour.

From the model presented in Fig. 1 it can be derived:

$$\alpha = \frac{w_o - w_t}{w_o - w_\infty} = \frac{V_o - V_t}{V_o} = \frac{a_o^3 - a_t^3}{a_o^3}, \quad \text{where}$$

V_o resp. a_o: Volume resp. geometrical dimension of the initial material

V_t resp. a_t: Volume resp. geometrical dimension of the actual non-decomposed material

a_t in turn can be expressed in terms of the velocity v_a of the phase boundary advancement along direction a and of the actual reaction time t:

$$a_t = a_o - 2v_a t$$

The conversion rate α accordingly is determined by:

$$\alpha = \frac{a_o^3 - (a_o - 2v_a t)^3}{a_o^3}$$

According to these theoretical considerations for the evaluation of specific reaction rates, e.g. v_a, from quantitative thermogravimetric measurements of the over-all weight-loss the following factors must be rationalized:

I

The total reaction time as well as the shape of the corresponding α/t or α/T plots are inherently dependent on the geometry of the sample.

II

Different velocities of the advancing phase boundaries along the directions of a given coordinate system influences the measured time-dependence of the over-all weight-loss. This fact is of particular importance if the course of the macroscopic reaction mechanism is controlled by a structural (topotactical) reaction mechanism.

III

Adsorption phenomena or the back-reaction of the gaseous product with the solid product often hinder a constant advancement of the phase boundary into the bulk. Influences of such diffusion processes are extremely difficult to detect by the sole evaluation of any α/t or α/T plots.

In addition the course of a decomposition process is strongly dependent on the chosen experimental conditions such as atmosphere pressure, heating rates of non-isothermal experiments, etc. It is therefore absolutely necessary to reassure the initially observed macroscopic reaction mechanism, whenever any experimental parameter is changed (ref.7).

EXPERIMENTAL

a) Decomposition of a solid metal complex

For the decomposition of many solid metal complexes consisting of molecular units of the stoichiometry $[M(X)_2(L)_4]$ (M: transition metal; X: Cl^-, SCN^-; L: NR_3, C_5H_5N, C_5H_4RN) a 'contracting volume' behaviour has been observed.

In the case of the decomposition of $[Ni(SCN)_2(C_5H_5N)_4]$ (refs. 8,9) to $[Ni(SCN)_2(C_5H_5N)_2]$ (refs.2,10) structural (Fig. 2), morphological (Fig. 3) and thermoanalytical investigations gave evidence for this macroscopic reaction mechanism.

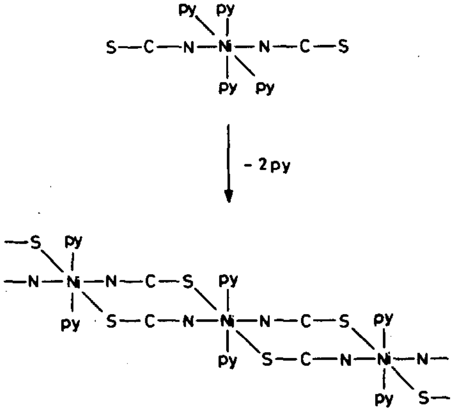

Fig. 2. Scheme of the structural reaction mechanism of the thermal decomposition of $[Ni(SCN)_2(C_5H_5N)_4]$ to $[Ni(SCN)_2(C_5H_5N)_2]$.

Quantitative thermogravimetric measurements under isothermal conditions using isolated $[Ni(SCN)_2(C_5H_5N)_4]$ single crystals of similar weights but exhibiting different shapes, e.g. plates, needles and cubes, definitely proved the correlation between time-dependent reaction course and geometry of the initial sample (Fig. 4).

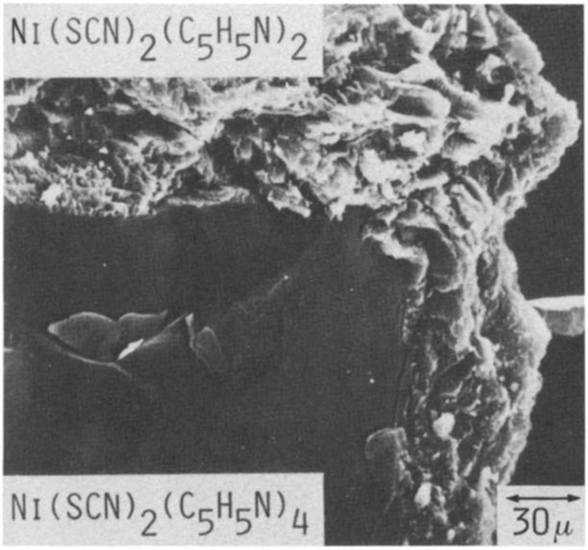

Fig. 3. Scanning electron micrograph of a section through a partially decomposed [$Ni(SCN)_2(C_5H_5N)_4$] single crystal.

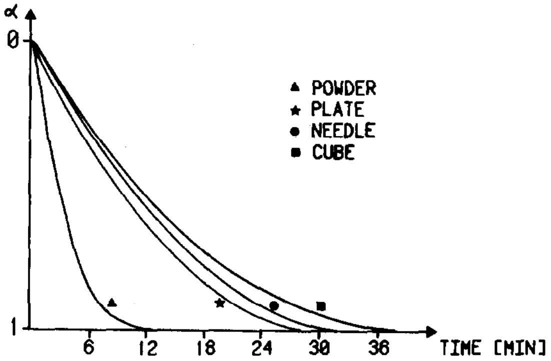

Fig. 4. Quantitative TG-measurements proving the influence of the crystal shape of the starting material onto the time dependence of the decomposition.

b) Decomposition of single crystalline calcite

If calcite single crystals are partially decomposed under high vacuum conditions ($p = 2 \cdot 10^{-5}$ mbar, T = 670°C) an extremely reactive calcium oxide product layer is formed on the entire surface of the initial crystal. For the morphological investigations (see Fig. 5 a-d) the partially decomposed samples have been exposed to CO_2 (T = 400°C) in order to form stable microcrystalline calcite again. Light - and scanning electron micrographs of sections through crystals treated by the experimental procedure mentioned above exhibit again the 'contracting volume' behaviour.

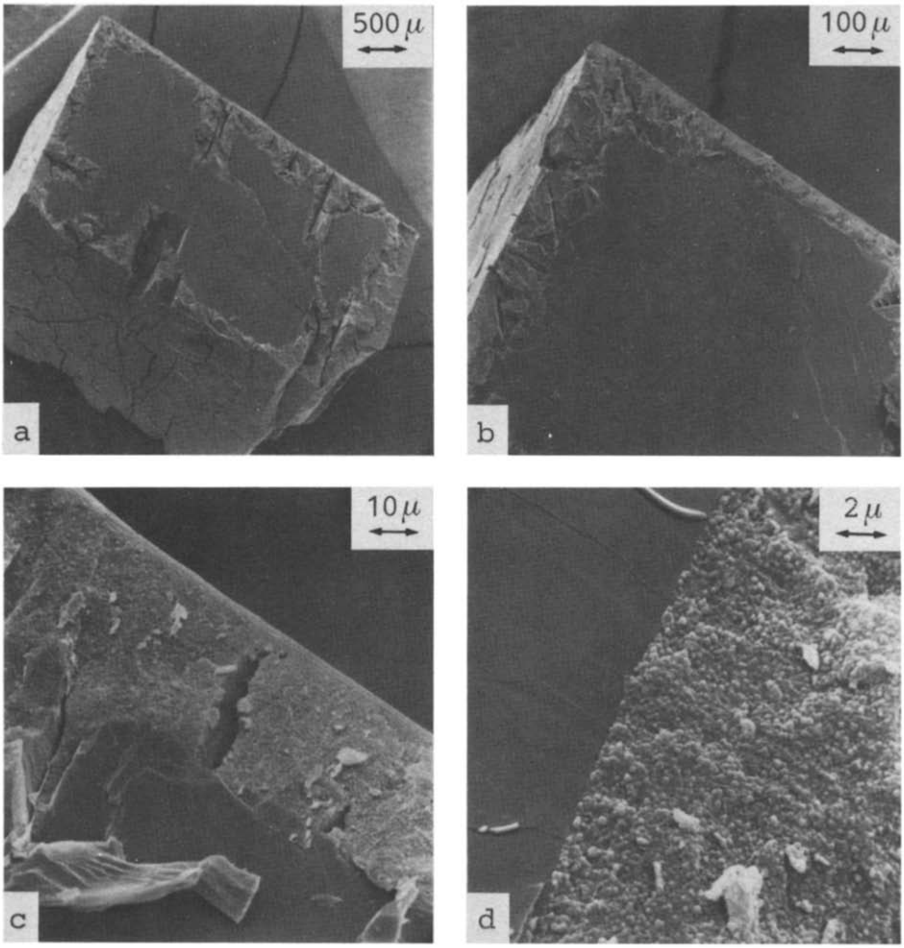

Fig. 5 a-d. Scanning electron micrographs of sections through a partially transformed calcite single crystal.

Even slight changes of the experimental conditions, e.g. from high vacuum to low partial pressures of N_2 or CO_2 during the decomposition process rigorously change the macroscopic reaction mechanism as shown in Fig. 6 (ref.11).

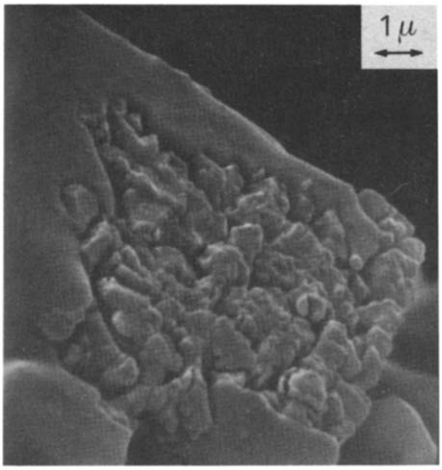

Fig. 6. Scanning electron micrograph of a calcite crystallite decomposed under N_2.

CONCLUSIONS

Decomposition reactions of solids represent a complex sum of simultaneously occurring (interdependent) processes. Whereas the evaluation of over-all measurements by means of theoretical models leads to mostly artificial, theory-dependent i.e. not reaction-specific kinetic data and, as a matter of fact, to rather ambiguous mechanistic models, the careful elucidation of the microscopic processes by independent quantitative as well as qualitative methods of investigation yield the framework for the understanding of the kinetics and mechanistics, i.e. the thermal behaviour or reactivity of solids in general.

In contrast to reactions in gases or solutions centres of reaction can be located within a decomposing solid and, therefore, the decomposition process itself has to be described with respect to the structure and morphology of the sample being investigated. In the case of a 'contracting volume' behaviour of a thermally decomposing solid the determination of the velocities of the initial material/product phase boundary advancement as function of carefully controlled experimental conditions and well defined directions yield preliminary specific kinetic data. This procedure allows, in addition, to discern between diffusion controlled and phase boundary reaction controlled processes, since diffusion phenomena caused by e.g. back-reactions of the gaseous product with the solid product manifest in a decrease of the velocity of the phase boundary movement with the increase of the product layer formed.

The knowledge of the occurring reaction steps such as bond breaks, formation of new bonds finally leads to a meaningful interpretation of the preliminary kinetic data and thus to reaction-specific, reproducible kinetic constants (ref.12).

REFERENCES

1 N. Lyakhov, A. Reller et al., to be published.
2 A. Reller, PhD Thesis, Zürich, 1981.
3 M. Maciejewski and H.R. Oswald, to be published.
4 B. Delmon, 'Introduction à la cinétique hétérogène', Technip, Paris, 1969.
5 R.K. Osterheld and P.R. Bloom, J. Phys. Chem. 82 (1978) 1591.
6 P. Vallet, 'Thermogravimétrie', Gauthier-Villars Editeurs, Paris, 1972.
7 N. Lyakhov, M. Maciejewski and A. Reller, to be published.
8 A. Meitzendorff, Ann. Phys. 56 (1842) 63.
9 M.A. Poraj-Koshits, Russ. J. Inorg. Chem. 4 (1959) 332.
10 E. Dubler, A. Reller and H.R. Oswald, Z. Krist. 161 (1982) 265
11 M. Maciejewski, work in progress.
12 A. Reller and H.R. Oswald, to be published.