*Journal of Thermal Analysis, Vol. 29 (1984) 1013–1016*

# EXPERIMENTAL APPROACH TO THE DETERMINATION OF MECHANISM AND KINETICS OF HETEROGENEOUS SOLID STATE REACTIONS $A_S \rightarrow B_S + C_G$

*A. Reller* and *H. R. Oswald*

INSTITUTE FOR INORGANIC CHEMISTRY, UNIVERSITY OF ZÜRICH,
WINTERTHURERSTRASSE 190, 8057 ZÜRICH, SWITZERLAND

Structural and morphological investigations of the solid state decomposition process of $Ni(SCN)_2(C_5H_5N)_4$ single crystals to microcrystalline $Ni(SCN)_2(C_5H_5N)_2$ reveal a contracting sphere reaction mechanism'. Reconsidering possible artefacts registered by quantitative thermoanalytical measurements a pathway for the determination of specific and reproducible kinetic parameters for the rate-limiting step is described.

The determination of mechanism and kinetics of heterogeneous solid state reactions by evaluating TG-measurements registered under non-isothermal conditions using more or less sophisticated mathematical procedures yields very often ambiguous and poorly reproducible results. As it will be presented in the following, careful investigations of heterogeneous processes ny means of selected independent experimental techniques, however, open up a promising pathway for the understanding of the interdependence of mechanism and kinetics/energetics of such reactions.

This contribution focusses on conclusions derived from investigations of the following solid state decomposition process:

$$Ni(SCN)_2(C_5H_5N)_4 \rightarrow Ni(SCN)_2(C_5H_5N)_2 + 2(C_5H_5N)$$

The structural reaction mechanism is characterized by the break of two $Ni-N(C_5H_5N)$ bonds per molecule of $Ni(SCN)_2(C_5H_5N)_4$ [1] and the subsequent formation of two Ni–S(SCN) bonds leading to the structure of $Ni(SCN)_2(C_5H_5N)_2$ [2, 3].

Investigations by means of X-ray techniques (Weissenberg and precession) using partly decomposed single crystals of the starting material gave no evidence for a topotactical structural reaction mechanism.

Results obtained by morphological investigations using light and scanning electron microscopy revealed that the reaction starts on the entire surface of the initial $Ni(SCN)_2(C_5H_5N)_4$ single crystal and the $Ni(SCN)_2(C_5H_5N)_4/Ni(SCN)_2(C_5H_5N)_2$ phase-boundary subsequently propagates into the bulk (see Fig. 1).

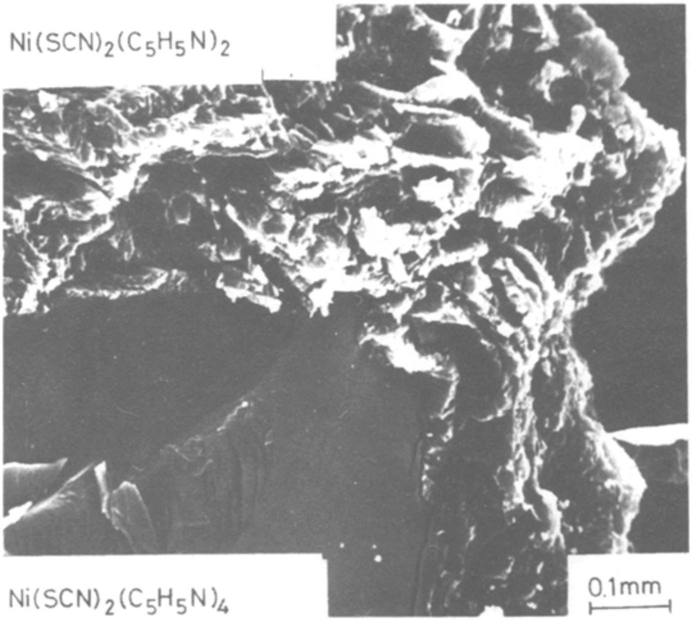

**Fig. 1** Scanning electron micrograph of a section through a partly decomposed single crystal of $Ni(SCN)_2(C_5H_5N)_4$

In a generalized form the macroscopic process can be described by a 'contracting sphere reaction mechanism': For an isolated single crystal of the starting material this mechanism can be expressed mathematically by the following equation [2, 4]:

$$\alpha = g\,\frac{a_0b_0c_0 - [(a_0 - v_at)(b_0 - v_bt)(c_0 - v_ct)]}{a_0b_0c_0}$$

where $g$: geometrical factor (depending on the shape of the initial single crystal); $a_0/b_0/c_0$: geometrical dimensions of the initial crystal at reaction time $t = 0$ (either orthogonalized coordinates chosen with respect to the crystal shape or defined crystallographic axes); $v_a/v_b/v_c$: velocities of the phase boundary propagations along $a, b$ and $c$ respectively into the reacting crystal.

It has been rationalized experimentally [5] and by model calculations, that the time-dependence of the over-all decomposition process of an isolated initial single crystal is strongly influenced by its morphology (see Fig. 2) and by the relative velocities of the phase boundary movements (see Fig. 3).

Furthermore measurements using several crystals or powder-like materials complicate any mathematical evaluation of meaningful kinetic data, since

$$\alpha_{\text{total}} = f\Big(\sum_{i=1}^{n} \alpha_i\Big)$$

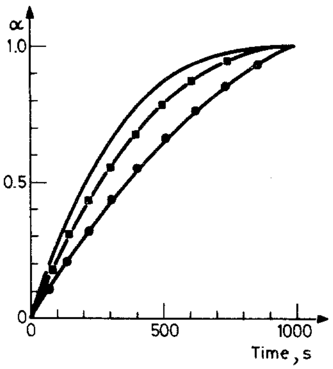

Fig. 2 Calculated $\alpha/t$ plots for the decomposition of initial crystals exposing different shapes [—— $V = a_0b_0c_0$ (cube); —■— $V = 3a_0b_0c_0$ (needle); —●— $V = 3a_0b_0c_0$ (plate); $a_0 = b_0 = c_0 = 2$ mm]

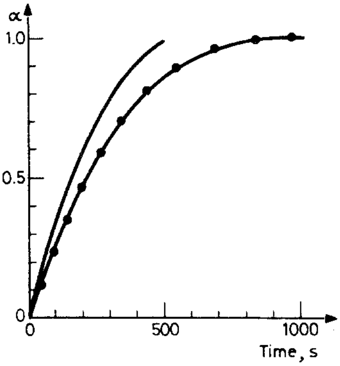

Fig. 3 Calculated $\alpha/t$ plots for the decomposition of cube-like initial crystals [—●— $v_a = v_b = v_c = 1 \cdot 10^{-3}$ mm/sec; —— $v_a = v_b = 1 \cdot 10^{-3}$ mm/sec and $v_c = 2 \cdot 10^{-3}$ mm/sec; $a_0 = b_0 = c_0 = 2$ mm]

where $n$ corresponds to the number of individual initial reactants. Since the well-known procedures for the evaluation of kinetics and mechanisms of solid-state decomposition processes are based on the time- resp. temperature-dependence (under non-isothermal conditions) of the over-all weight-loss the resulting data such as activation energies' or 'orders of reaction' are rather a consequence of experimental conditions and mathematical algorithms than reaction-specific values.

Which are reasonable pathways for a more promising approach to a deeper insight into such complex processes?

Starting with compositionally and structurally well defined systems, preferably single crystalline materials, the decomposition process has to be fully characterized with respect to the formation of all solid and volatile products. The elucidation of the structural (topotactical) reaction mechanism yields further information about the elementary processes including possible reversible steps. Together with careful observations of morphological changes such as growth of nuclei, propagation of phase boundaries within the given structural framework as well as influences of the actual experimental conditions on the formation of the product phase, the micro- and macroscopic reaction mechanism can be determined.

This ensemble of merely qualitative experimental investigations represents the prerequisites for the quantitative determination of the kinetic parameters of the rate-limiting process: From the time- and temperature-dependent propagation of initial material/product phase boundaries along well-defined directions — this is obviously dependent on the more or less topotactical structural reaction mechanism — the rate-limiting elementary process as well as its rate-constant can be evaluated (see e.g. [6, 7]). From isothermal experiments performed at different temperatures reproducible quantitative data for the 'activation energy' of the rate-limiting reaction step are accessible.

## References

1 M. A. Poraj-Koshits, Russ. J. of Inorg. Chem., 4 (1959) 332.
2 A. Reller, Ph. D. Thesis, University of Zürich, 1981.
3 E. Dubler, A. Reller and H. R. Oswald, Z. Kristallogr., 161 (1982) 265.
4 B. Delmon, Introduction à la cinétique hétérogène, Technip, Paris, 1969.
5 H. R. Oswald, A. Reller and M. Maciejewski, Thermochim. Acta, 72 (1984) 139.
6 N. Lyakhov, A. Reller et al., in preparation.
7 A. Reller and H. R. Oswald, to be submitted.

**Zusammenfassung** — Strukturelle und morphologische Untersuchungen der Zersetzung von $Ni(SCN)_2(C_5H_5N)_4$-Einkristallen zu polykristallinem $Ni(SCN)_2(C_5H_5N)_2$ haben gezeigt, daß diese Festkörperreaktion nach einem "Kugelkontraktions—Reaktionsmechanismus" verläuft. Unter Berücksichtigung der bei quantitativen thermoanalytischen Messungen möglicherweise auftretenden Artefakte wurde ein Weg zur Bestimmung der spezifischen und reproduzierbaren kinetischen Parameter für den geschwindigkeitsbestimmenden Schritt aufgezeigt.

**Резюме** — Структурные и морфологические исследования твердотельного процесса разложения монокристаллов комплекса $Ni(SCN)_2(C_5H_5N)_4$ до микрокристаллического $Ni(SCN)_2(C_5H_5N)_2$ обнаружили "механизм реакции типа сжимаемой сферы". Пересматривая заново факты, отмеченные на основе количественных термоаналитических измерений, описан путь определения специфических и воспроизводимых кинетических параметров для стадии, определяющей скорость реакции.