

EXPERIMENTALLY AVAILABLE KINETIC CODES AS A TOOL FOR PROMISING DATA EXTRACTION IN THERMAL ANALYSIS

E. Koch

MAX-PLANCK-INSTITUT FÜR STRAHLENCHEMIE, STIFTSRASSE 34-36, D-4330
MÜLHEIM AN DER RUHR, F.R.G.

By the study of 3000 kinetic runs for all homogeneous two-step models under variation of activation and signal parameters, it has been stated that the generated Mechanistic Concentration Code (= MCC) is the best vehicle for data extraction in Thermal Analysis. It summarises the rate-controlling steps and their molecularities, independently of their activation data and (to 80-90%) of their method-specific signal parameters. Hence, an optimum evaluation needs the internal (best-fitted) reference step, the initial concentration of a reference reactant, and equal weight of theoretical and experimental results, reached using the same algorithms. Thus, the MCC of any series measured in general allows for a reliable model determination via the distribution into all two-step models, using the tools of probability and decision theory. A transfer of the strategy to heterogeneous reactions is discussed.

Keywords: kinetic codes, Mechanistic Concentration Code

Introduction

Even the kineticist working in Thermal Analysis has to deal with an exponentially growing amount of data, often generated by a computer program which has a black box character for him [1]. However, increasing information may not necessarily increase our knowledge if it is not filtered in an appropriate way; the consequence could be 'information chaos': Too much data on the screen may confuse the user, although the computer may need it for its final conclusions.

In the last twenty years, I have developed a classifying system of two kinetic coordinates, based on asymmetry and halfwidth (or relative height, cf. [2, 3]) of a signal curve, referred to the activation data of a reference reaction: The shape index S and the reaction type index M . In a Cartesian

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representation of these coordinates vs. each other, all elementary reactions correspond to two invariant points (for molecularity 1 or 2), whilst complex reactions reveal typical regions of the respective reaction mechanisms which include one or both of these points as limiting cases.

In the case of complex processes, the kinetic point obtained so may depend on the activation data of the further steps, referred to those of the first reaction, the reference reaction.

The Mechanistic Concentration Code as an information carrier

But this dependence can be removed by introducing a $3 \times N$ -matrix (=MCC), which describes in its three lines the general kinetic behaviour of the system, reflected by the three response parameters, S , $M(\text{init})$ and $M(\text{overall})$ in the form of N elements. These belong to intervals of an appropriate condition parameter, here the starting concentration of a suitable reactant in a series.

The task of creating the three strings of such a MCC can be delegated to a computer, which needs two tolerance values: The first for the installation of adequate intervals defining the concentration ranges, the second for the fixation of the corresponding 'behaviour elements'. These may indicate variability ('+' = increasing or '-' = decreasing) or constancy ('C') of the response parameter; in the latter case, the symbols may denote the order, that is the apparent molecularity of the respective rate-determining step revealing the cases Low, 1, Medium, 2, and High. Such MCC's can be determined both for experimental and for theoretical plots, using the same software for the evaluation; records according to very different thermoanalytical techniques may be encoded. Then, the numerical expenditure is minimum if the derivative signal can be considered as the sum of measuring quantities proportional to the rate in the particular steps of the reaction scheme. I will call such a method a linear thermoanalytical method, especially if validity of the Arrhenius equation is assumed [4, 5, 6].

But also results from rather complicated techniques such as DTA may be encoded, after the temporary overall rate has been calculated by the use of the respective transport equation – here the TIAN-CALVET equation. For the determination of the kinetic coordinates using adequate equipment, the problem of deconvolution has been solved by applying semi-empirical expressions, proposed in 1976 and 1978 by Koch and Stalkerieg [7, 8].

Theorem of Common Kinetic Runs

That a MCC really represents a nearly unambiguous description of a kinetic model in practical kinetic work, has become obvious since 1978 [9]. In a computer project, performed on 3000 generated curves of 250 series of all homogeneous two-step models, it was found that, for a linear method, a 'Theorem of Common Kinetic Runs' may be applied [10]: A MCC is independent of the activation data of both steps of all such models; furthermore, it is even approximately independent of their signal parameters (e.g. enthalpies). All MCCs obtained reveal a common architecture and involve three types of behaviour elements:

1. The two limiting elements (for lowest and highest starting concentration) indicate constancy, i.e. an invariant from which the molecularity (or formal order) of the two source reactions can be determined (1,2 or fractional = L , M or H).

2. The main elements between ('+' or '-') are similarly characteristic of the model.

3. The rest elements describe a residual dependence on the signal parameter ratio, but their contribution to the total (~760) elements of all two-step models were less than 10% for parallel and less than 16% for consecutive reactions.

Thus, the Theorem of Common Kinetic Runs is approximately valid. Consequently, from the MCC of an experimental concentration series, easily obtained using a linear TA method and a linear rating equation as described [11], a list of the best fitted two-step models can be obtained by comparing the experimental MCC with the MCC's of all models in a data bank.

Example of a homogeneous reaction

In order to test such a procedure, the reaction between triphenylphosphine with its ozonide in CH_2Cl_2 (starting above ca. 180 K) and its decomposition reaction (above 235 K) [12] were re-investigated. Six models were developed, beginning with the scavenger reaction as reference reaction, which was continuously extended, ending at a plausible seven-step model [13]. The activation parameters of all steps had been adapted to the experiments. Then, the comparison of the generated seven theoretical MCCs with the experimental MCC reveals that the six-step and the seven-step models show the best fit; on the other hand, if we compare the theoretical MCCs with each other, it becomes obvious that precisely that two-step model just

formed by adding a step to the previous model shows the highest probability (Fig. 1). This confirms the capability of the new concept for generally determining also rather complicated kinetic models.

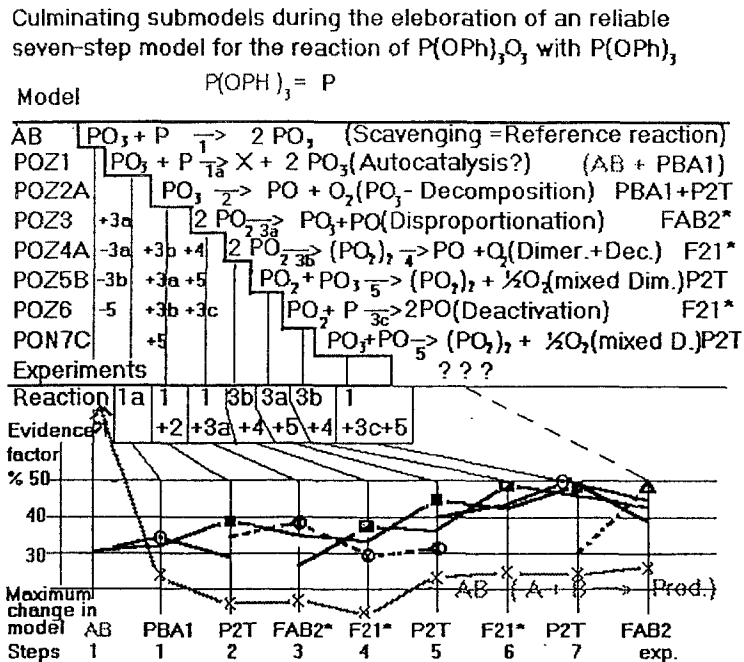


Fig. 1

For models with more than two steps, a systematic translation of the MCC into the true model hitherto seems to be too complicated. However, this problem is similar to that of chess computer programs, because the number of steps corresponds to the search depth. Since international chess champions have recently been defeated by chess computers, I assume that also in reaction kinetics the combinatorial variety will be ruled in future by respective programs [9, 14].

Nevertheless, we can at least compare the MCC of a rather complex reaction – for example, the oscillative Belousov-Zhabotinsky reaction – with the theoretical codes for any multi-step model assumed, in order to see whether it is better than others. In this way, we have stated that our nine-step model [15] is much better than the simplest model capable of oscillations, the five-step OREGONATOR.

Conclusions

1. For a successful model research, elements representing kinetic behaviour modes of order-defining Meta-Parameters are much more useful than activation parameters, rate constants or correlation coefficients. Obviously, the best and simplest vehicle for characterizing the kinetics of homogeneous complex processes is the MCC. This matrix meets very well the requirements of a satisfactory data extraction and, therefore, should provide for a better reliability of kinetic data, an aim intensively followed by the ICTA KINETICS COMMITTEE [16, 17]. A MCC describes both the rate-determining steps by listing their molecularity, and the type of dependence of the reaction rate on the concentration, in the simplest possible manner. Furthermore, the concepts of the initial and the overall rate are taken into account, because the second and the third line of an MCC are based on the initial and on the overall reaction type index. These aspects are fundamental for any kinetic interpretation; the global activation energy [4], although questionable in its meaning, is the first easily available parameter describing the temperature effects on the rate.

2. Reference evaluation concepts, based on a reference reactant and a reference reaction, and capable of directly comparing theory with practice, will become similarly important as the sample-reference concept for thermoanalytical equipment. It is evident that a self-correcting strategy, based on the natural existence of invariant data, renders the strongest tool for clarifying a kinetic problem.

3. The involvement of probability and decision theory [18, 19] should improve the solidity of kinetic interpretation at all and make possible quantitative comparisons of different ideas of models. As the simplest concept, the linear contribution of elemental charges per concentration interval (1 for agreement, 0 for disagreement) for the compared three strings of the experimental MCC with the theoretical one is proposed which is already very effective [11].

4. Transfer of the strategy to heterogeneous kinetics should be promising, if the concentration is replaced by another adequate condition parameter, and if a general principle for the classification of solid-phase reactions [20–23], capable of including more than one basic process, will have been established. Indeed, a computer knows less than the experimenter and has, therefore, at least to be informed how the final consequences have to be displayed. Reliable classification principles have always been fundamental for any progress in the natural sciences; therefore, the *S*- and *M*-coordinates could play a similar role as in homogeneous kinetics [24].

5. Special variants of commercial equipment [25] should be more adapted to the needs of determining the curve-specific kinetic meta-parameters under elimination of heat-transfer kinetics; the latter contribution is rather caused by the measuring principle than by the reaction itself.

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Zusammenfassung – Durch die Untersuchung von über 3000 kinetischen Abläufen für alle homogenkinetischen Zweistufen-Modelle wurde festgestellt, daß der Mechanistische Konzentrations-Code (=MCC) ein optimaler Datenträger in der Thermischen Analyse ist: Er beschreibt die geschwindigkeitsbestimmenden Schritte und ihre Molekularität, unabhängig von deren Aktivierungsdaten und, zu 80–90%, von ihren methodenspezifischen Signalparametern. Ein optimales Auswerteverfahren benötigt einen internen (optimal angepaßten) Referenzschritt, die Startkonzentration eines Referenz-Reaktanten und Gleichberechtigung theoretischer und experimenteller Befunde, erreicht, durch Verwendung derselben Algorithmen. Allgemein ermöglicht der MCC aus einer Reihe von Experimenten dann eine Modellbestimmung über eine Verteilung, die durch entscheidungstheoretische Kriterien die Wahrscheinlichkeiten aller Zweistufenmodelle auflistet.

Eine Übertragung des Verfahrens auf heterogene Prozesse wird diskutiert.