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THE PROBLEM OF "INVERSE REACTION KINETICS" UNDER THE ASPECT OF CALORIMETRIC MEASUREMENTS

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Abstract. It is shown that the DTA method performed in a twin stirring-type apparatus has a good chance to successfully meet with the problems of "Inverse Reaction Kinetics", i.e. to find out an appropriate reaction mechanism including the prevailing activation data of the particular steps for a reacting system studied. Although experimental signal curves can be reproduced using a suitable model and integrating the system of differential equations involved, other ways have to be used for a less tedious approach to the best mechanism.

In order to develop adequate diagnostic criteria, the informative potential of different parameters obtained by a simple first/second order evaluation program is studied. For complex processes in solution, the dependencies of such parameters on the initial reactant concentration or on the heating rate often reveal periods of constancy which indicate the rate-determining steps of the mechanism. Based on concentration series of DTA experiments applied to twenty different systems, the following order of increasing kinetic utility of the parameters was found by comparing the number of these occurring periods of constancy:

> Peak temperature < Overall enthalpy < Initial activation energy < Overall activation energy < Final temperature < Initial A-factor < Relative signal height < Overall A-factor ≤ Initial temperature < Initial reaction type index < Shape index < Overall reaction type index.

By these results, my earlier theoretically founded assumption has been confirmed that the "mechanistic indices" are the best quantities to reveal the reaction mechanism of any reacting system studied.

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INTRODUCTION

The term "Inverse Reaction Kinetics" describes the problem of recognizing the prevailing reaction mechanism for a reaction studied and determining the activation data of the particular steps [1].

Since, in general, chemical processes are accompanied by production or consumption of heat, and since the rates of most thermal reactions are temperature-dependent, the temperature-programmed calorimetry seems to be a method focussed on this aim. Especially the DTA applied in a stirring-type apparatus as was developped by the author was proven to give satisfactory results in chemical studies [2-4].

DOUBLEFOLD ROLE OF CALORIMETRY

If we assume

1) a first-order heat decay law between stirred sample and the temperatur-defined environment
2) Proportionality between conversion rate and heat-flow generated by the reaction
3) Constancy and equality of the heat capacities of sample and reference ,

it has been proven that in an apparatus as mentioned above, the experimental DTA curves of elementary reactions obey Newton´s law for the heat balance, the rate law and the Arrhenius equation. This was directly confirmed by comparison of such curves with theoretical DTA curves [5,6].

DTA curves obtained under such conditions show features between two limiting cases. If the cell constant c of the equipment and/or the specific time u [7,8] of the reaction are very low, the system may behave as in an adiabatic calorimeter: There is no heat exchange with the environment, and the temperature difference must converge to a final,asymptotical value. The type of the curve is integral with respect to the reaction rate.

In the opposite case (high c- and/or u-value), the limiting curve has a derivative form and a maximum, but the temperature difference tends toward zero since the heat is completely removed from the sample. Conditions approaching to the first case are appropiate for an enthalpic measurement, whereas in the second case,apart from the problem of sensitivity, kinetic studies may be favoured. Real DTA curves show features between both extreme cases, and the extent of kinetic information to be extracted is increased by the enhancement of product u·c [6,7].

SIGNALS OF COMPLEX PROCESSES AND THEIR THEORETICAL REPRODUCTION

If we consider a system of p reactions, signal curves y(t) which represent the time plot of the derivative of any physical quantity x(t) may for many methods of investigation be formulated as

$$y = \frac{dx}{dt} = \sum_{i=1}^{p} \lambda_i \cdot k_i[T(t)] \cdot \pi_i(t) \qquad (1)$$

λ_i is an indication parameter typical of the method which represents the total change of x in the particular step i; k_i is the rate coefficient which varies with temperature due to the temperature program T(t), and π_i is a concentration (unimolecular step) or a product of two concentrations (bimolecular step). The product $k_i \cdot \pi_i$ characterizes the internal kinetics.

For DTA, λ_i is the ratio enthalpy/heat capacity, but the signal curve observed is obtained from the conversion curve (1) using the heat balance equation and the prevailing cell constant [2,4].

From theory, it is evident that a linear temperature increase as used in DTA offers the best conditions for the kinetic analysis of complex systems [8,9]. Using this prerequisite, for an elementary process the product $k \cdot t$ in the exponent of the time-resolved isothermal rate law is substituted for by product $u(t) \cdot k(t)$ where $u(t)$ may be approximately constant compared with the rapidly increasing rate coefficient. Thus, $u(t)$ at the maximum,which we call specific time u_m ,is always the same fraction of the halfwidth h of the temporal rate signal for a certain reaction order. Hence, I have defined a reaction-type index M which is available from the halfwidth and the activation data E and k_∞ of a reference reaction, which may be the initiating reaction or the overall reaction (order n; R = gas constant):

$$M = \frac{E}{h\,(\lg k_\infty + \lg u)^2} = \frac{R}{\lg^2 e \cdot 2.25 \cdot n^{0.52}} \qquad (2)$$

As the shape index S [9], the M-index shows univariant values for an elementary process and exclusively depends on the reaction order.

Koch and Stilkerieg [7] have proposed expressions for the mechanistic coordinates S and M using the quantities u_m, c and the maximum temperature difference ϑ_m in order to exclude the influence of heat decay and temperature feedback from the DTA-related data.

Assuming validity of eq. (1) and of the Arrhenius equation for all steps involved in a complex reaction, DTA signals obtained by adequate equipment may be readily reproduced theoretically when the true mechanism and the activation data are known, since effective integration subroutines also adapted to "stiff" problems have dedelopped in the last decade [10,11]. However, because of the great number of parameters to be expected, such a procedure if directed to data fit is too tedious to be a reliable tool for revealing a complicated reaction mechanism.

The morphology of derivative signal curves according to eq. (1)

shows various relationships to the mechanism of a reaction.Parameters as the total number of peaks (= number of reactions) , initial temperature (= unimolecular or bimolecular reaction?), and relative signal height (= kinetic flux, i.e. type of branching in previous reactions) offer direct information about the reaction mechanism. Therefore, a classification table for reaction mechanisms can be constructed which for overlapping peaks may be refined by the mechanistic coordinates S and M [12,13].

INTERPRETATION OF SIGNAL CURVES USING CONCENTRATION SERIES

A simple, but very effective and general procedure for the elucidation of the reaction mechanism is a kinetic evaluation based on a rate law of first or second order. If the mechanistic coordinates obtained suggest an elementary process, the other parameters must characterize the process directly. However, if they indicate a complex process, plots of many sorts of parameters versus initial concentration of reactant or heating rate, respectively, will give information about the true mechanism. In order to test the informative potential of readily available parameters such as initial temperature, overall or initial activation data etc., we have evaluated experimental DTA curves which involve ∿100 different reacting systems in solution. A package of interactive computer programs for evaluation, simulation and search was developped which communicates with a data library containing plot files of 1100 particular DTA (and u.v.) experiments including input and result parameters. Either the agreement of experimental and theoretical signal curves or any desired parameter correlation curves can be represented graphically [13,14].

Series of experiments based on varying initial concentrations of the reactants reveal typical correlation curves for nearly all parameters. These may show one or several periods of parameter constancy indicating that the kinetic behaviour of the system corresponds to <u>one</u> rate-determining step in that range of the initial concentration. For consecutive processes, these periods of constancy reflect the stationarity of the concentration of a certain intermediate, whereas in the other cases they simply indicate that the starting product is preferentially consumed by only one of competitive processes of different order.

Table 1 shows the contributions of such periods of constancy for the different patterns of constant/variable sequences observed which is considered for the 13 most important parameters. This statistical survey is based on 20 series involving such reactions as decomposition of diazonium salts, unstable peroxides or sulfoxides, oxidation reactions ($(OC_6H_5)_3PO_3$ + Dienes, $KMnO_4$+ Malonic acid, $NaIO_3 + H_2O_2$), Belousov-Zhabotinsky-type oscillating reactions ($Br^- + BrO_3^-$ + Malonic acid in aequ. H_2SO_4 + catalyst: Ferroin, $MnSO_4$, $Ce(SO_4)_2$, $CeCl_3 \cdot 6H_2O$) and their subsystems, as $Br^- + BrO_3^-$, $Ce(SO_4)_2$+ Malonic acid etc.. In the last row of the table, the total contribution of the number of periods of constancy referred to the number of possible periods at all (10 in 7 different patterns) was calculated for all parameters by summation. This valuating quantity represents the utility of that parameter for a diagnosis of the reaction mechanism.

From the order of valuation presented in table 1 it has to be concluded that the mechanistic coordinates S, M (referred to the overall reaction) and M_0 (referred to the initial reaction) offer the best chances to be used for a reaction diagnosis, whereas quantities as overall enthalpy and peak temperature, though readily to be determined, are not very useful in this respect.

pattern	parameters											
	M	S	M_0	T_0	k_∞	O_{rel}	$k_{\infty 0}$	T_e	E	E_0	ΔH	T_m
c	1	1	1	1	1	1	0.5	1	1	1	0.75	0.74
-c(-)	1	1	1	1	1	0.84	0.84	0	0.67	0.5	1	0
(c)-c	1 1	1 1	1 1	1 1	1 1	1 0	1 1	1 1	0 1	0 1	0 1	1 0
-c-c-	1 1	1 1	1 0	0 1	1 0	1 1	0 1	0.5 1	1 0	1 0	0 1	1 1
c - c	0.71 0.87	0.67 0.67	0.58 0.80	0.58 0.87	0.96 0.79	0.5 0.87	0.92 0.75	0.72 0.54	0.71 0.67	1 0.67	0.72 1	0.54 0.75
- c - c	0.83 1	0.83 1	1 1	1 0.67	0.33 1	0.83 1	0.5 1	0.83 0.83	1 1	0.83 1	0.67 0.67	0.67 1
valuation index	0.94	0.92	0.84	0.81	0.81	0.80	0.76	0.74	0.71	0.70	0.68	0.67

Table 1 Occurrence of periods of constancy in the concentration plots of various parameters (10 series/ca.100 DTA curves)

First column: c = period of constancy ; - = no constancy

Other columns: 0 = no c-periods are present; 1 = all c-periods are present

Ambigious cases are considered by half weight; abbreviations of parameters: see abstract

INFLUENCE OF THE HEATING RATE

Apart from the initial concentration of reactants, the heating rate is a fundamental parameter of reaction conditions in non-isothermal kinetics. Variation of this time-related quantity may lead to peak-dissection effects even for reactions of the same order [1,15].

On the other hand, experiments at low heating rates are lengthy which gives away some of the elegance and rapidity of temperature-programmed experiments. Such studies require another kind of organization compared with concentration series so that the majority of information on this area is stemming from computer studies. Thus, computer reconstructions of the signal curves of two-reaction models have revealed that the possible basic mechanisms lead to characteristic trends of the mechanistic coordinates for very low or very high heating rates, respectively [9,16]. Depending on the order of the elementary substeps, an asymptotic approach to the first-order or second-order value is observed. Results of 15 experimental series with systems similar as above indicate that for S, M and other parameters, such as E_0, E, - ΔH and T_0, several periods of constancy may appear if two or more reactions are to be supposed to participate in the process.

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