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NON-ISOTHERMAL REACTION KINETICS. VI. EXPERIMENTAL TWO-STEP AND FOUR-STEP MODELS IN SOLUTION CHEMISTRY

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ABSTRACT

The kinetics involved in thermoanalytical curves can be interpreted by the comparison of experimentally available information strings with those of theoretical models stored in a data bank. Such kinetic codes are based on the dependence of the mechanistic coordinates on the initial concentration of a reactant. Some general and some special results obtained with a computer program, applied to 100 series of different reactions in solution, are presented. The program distributes all of the possible two-step models, sorted with respect to the probability of their occurrence. Similarly, all possibilities of a superposition of two such models, the first more valid for low, the second for high initial concentrations, can be determined.

The theoretical foundations for such a program and the obtained interpretations are compared, for some examples, with mechanisms proposed in the literature. The general correlations between the various parameters referring to the probabilities of the models confirm the utility of the new concept.

INTRODUCTION

The ultimate aim of reaction kinetics is to determine the mechanism governing a reaction under investigation. Often, however, the argument is presented that a kinetic study is not capable of establishing a certain mechanism, only of rejecting false models.

Utilizing the impressive progress in measuring techniques, as well as data processing and the corresponding improvements in temperature-programmed kinetic methods, this paper examines whether or not the best mechanism can be determined from a given list.

Thermal analysis can help in the direct study of not only "slow", but also some of the "fast" chemical reactions: apart from using small starting concentrations, it is the concept of raising the temperature from the very minimum that may shift the rate down to the conventional time range [1,2], especially for reactions of considerable activation energy. Furthermore, an essential section of mechanisms, including both slow and fast steps, also permits the evaluation of fast processes [3]. The results obtained from such a complicated model as the oscillatory Belousov–Zhabotinsky reaction, which was studied by DTA and temperature-programmed UV reaction spectroscopy, may serve as an instructive example [4]. For reactions in solution, at least, there are numerous indications that the saving in time [5] is by no means the only advantage of non-isothermal over isothermal methods [6,7].

Promising strategies for elucidating complex mechanisms are based on the idea of combining pattern recognition methods with the capability of modern integration programs [8–10]. In line with our investigations on the theory and practice of elementary processes, a systematic approach is attempted to the obvious next step, the superposition of two or even more reactions which obey the law of mass action. Based on utility theory [11], the computer program MODEL was written in order to classify the kinetic results of some one thousand experiments involving different reactions in solution. The general "fingerprint" method presented here opens a direct way to systematic kinetic analysis of chemical reactions.

DEVELOPMENT OF IDENTIFICATION MATRICES

In order to correlate an assumed kinetic model with the results of a number of experiments as unambiguously as possible, several response parameters, which are adequately sensitive to the type of kinetics, were selected. Furthermore, a condition-defining transmitter parameter was changed in a series of experiments. In solution or gas phase it is usual to study the effect of the starting concentration of one reactant—this was also the approach in our last study [4]. The total initial concentration range for all the experiments was divided into several intervals, in order to combine measuring points where the type of behaviour of the response parameter is maintained (Fig. 1). In other words, the information obtained was split into a sequence, ordered with respect to the dependence on the transmitter parameter.

Therefore, a matrix was defined in such a way that the rows correspond to the response parameters and the columns enumerate the concentration intervals, beginning with a self-selected $c(\mathrm{min})$, and ending with a corresponding $c(\mathrm{max})$. The discussion in this paper will be restricted to the three most effective response parameters, the mechanistic coordinates [12,13]; therefore the first, second and third (last) row correspond to the corrected shape index (S), the initial ($M10$ or $M20$) and the overall reaction type index ($M1$ or $M2$) respectively.

Mechanistic concentration codes and logical concentration intervals

The mechanistic concentration code (MCC) [4,14,15], expressed by three information strings, describes the prevailing kinetics, in the light of a

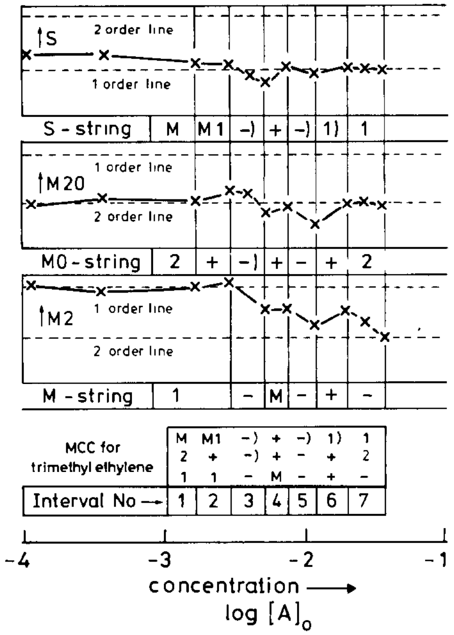

Fig. 1. Scheme of code generation for series 8 of Tables 3 and 4; concentration of 1-methylbutene(-2) is varied; 12 experiments at 11 concentrations. Parameters: *S*, shape index; M20, initial reaction type index (referred to second-order); M2, overall reaction type index. Code symbols: M1, limit range between M and 1 (M preferred); M), −) etc., not very distinct, perhaps constant.

particular reactand. However, the places in this identification matrix are not occupied by the actual values of the mechanistic coordinates but by symbols reflecting their behaviour with respect to dependence on the logarithm of the initial concentration of the respective reactant: increasing, +, decreasing, −, or constant, C. For the C elements of the MCCs, which indicate rate-determining steps, logical and numerical information can be combined. In this case, a symbol more specific than C is used which indicates the corresponding value or range of the temporal reaction order in this interval, referred to a hypothetical reference step. The integer values 1 or 2 indicate the molecularity, partitioning three ranges of a formal reaction order. Therefore, the C symbols are classified, using "order" elements: L (Low) < 1 < M (Medium) < 2 < H (High) [2,12–14].

A computer program was written in order to automatically determine the limits of the concentration intervals required. Considering two neighbouring points in the sense of increased initial concentration (Fig. 1), the new symbol is derived from the position of the second point, compared with that tolerance interval [14] which is defined by the first point: if the new value of the response parameter is inside these limits, the element is C (or L, 1, etc.), whereas a position below or above the limits is indicated by − or +, respectively. If the next point leads to a different symbol, a new concentration interval is opened beginning with the foregoing point, whereas in the opposite case the interval is extended. This procedure is repeated until $c(\max)$ has been reached.

Mechanistic matrix

A preliminary determination of the MCC, consisting of three such information strings, requires the separate calculation of their concentration limits. Then, the interval limits of the string with the most intervals are defined as representative for the other two strings, i.e. the determination of the elements has to be repeated, but based on these common concentration limits. In the case of an occasional partial disagreement of the limits, this procedure may lead to some overlapping intervals and to a violation of the concept above; but the advantage is that the results are then represented in a rectangular $3 \times q_{ex}$ matrix, where q_{ex} is the number of intervals (spaces) which can be compared with analogous matrices of theoretical models.

Generation of a set of two-reaction codes

In order to arrive at a computer-consistent terminology of all models obtained from two-reaction steps, four basic types of mechanism were defined [2]: independent, U, (Unabhängige Reaktionen), concurrent, P, (Parallelreaktionen), consecutive, F, (Folgereaktionen) and opposing, G, (Gegenreaktionen) reactions. The numbers appended refer to the two steps representing their molecularity types: unimolecular (index 1), and bimolecular reactions (index, AB for different, and 2 for equal, initial concentrations of the reactants). In this way, the following 26 models are obtained.

1. X11, X12, X22, X1AB, X2AB;X = U or P
2. Y11, Y12, Y21, Y22, Y1AB, Y2AB, YAB1, YAB2;Y = F or G

The first index identifies the initiating reaction occurring at the lower temperature and taken as the reference reaction. If recoupling of the reactant with a reaction product is also considered, two special models have to be included.

P1A;$A \rightarrow B \xrightarrow{+A}$ products

and

P2A;$A \xrightarrow{+A} B \xrightarrow{+A}$ products

As described in our recent papers [12,13], for the calculation of the reaction type index, a reference reaction is needed, i.e. if one differentiates between an initial and an overall kinetics evaluation, four indices exist for the two possible molecularities, M10, M1, M20 and M2. Thus, the model list has to be extended by those U and P types which show the reverse indices, i.e. X21, XAB1 and XAB2; X = U or P. However, all U types and models with equal indices are omitted here; the codes of the latter show one constant element only in every row [12,16].

Because of the slight modifications in the codes, we differentiate between models where the activation energy of the step defined by the second index,

TABLE 1

Mechanistic concentration codes (MCC's) of some two-reaction models

Model (string length)	MCC	Alternative mode	MCC
1: $A \rightarrow P$ (1)	`1` `1` `1`	2: $2A \rightarrow P$	`2` `2` `2`

AB: $A+B \rightarrow P$
 	
(4)
	`1 + - 1`
	`1 - + M`
	`1 - + 1`
		G21: $2A \rightleftarrows B$	`L + + 2`
			`1 - - 2`
			`2 + - 2H`

P12: $A \rightarrow P$
$+A \searrow$
(5) $P1$
	`1 +)+ - 2`
	`1 - - - 2`
	`1 - M)+ L1`
		G12*: $A \rightleftarrows 2B$
		
		+6 other models
			`1 +)+ + +`
			`1 1 1 +)-`
			`1 + + + -`

P1A*: $A \rightarrow B$
$+B \searrow$
(6) $P1$
$E_1 > E_2$
	`1 +)+ M - 1M`
	`1 1)+ L)- 1`
	`1 1L- 1 1 1`
		FAB1: $A+B \rightarrow C \rightarrow P$
		
		+6 other models
			`L -)L -)+ H)`
			`1 1 - - - H)`
			`1 - -)- 2 2`

P1A: $A \rightarrow B$
$+B \searrow$
(7) $P1$
$E_2 > E_1$
	`- - 1 + 1 1 1`
	`1 + L)- 1M1M1M`
	`1 + + L)- +)1`
		PBA1: $A \xrightarrow{+B} P$ [a]
		$\searrow$
		$P1$
		+4 other models
			`M 1)1 +)+ - 1`
			`H + + + 2 + 1`
			`1 1)1 - M)- 1`

1A: $A+B \rightarrow 2B$
 	
(8)
	`M - - - - 1 1 1`
	`L +)-)+ - L)- 1`
	`1 +)-)+ - M)+ 1`
		PAB1*: $A \xrightarrow{+B} P$
		$\searrow P1$
		+3 other models
			`1 1 + H)-)- + 1M`
			`1 1L- + -)H + 2M`
			`1 1 - M)-)M + 1`

F21: $2A \rightarrow B \rightarrow P$
 	
(9)
	`2M+ - M - L + M11`
	`2)+)+ L - 1 +)-)L)`
	`2 2 +)1)+ +)L)+)L)`
		No further models	

These are some examples arbitrarily taken from the TRM model set (32 models) and arranged for increasing string length. All information elements use two spaces; thus, double symbols indicate domains between two main ranges (L, 1, M, 2, and H) where the first symbol means to the closest range (e.g. 1M = nearly first-order, M1 = considerably above first-order, etc.). The symbol) in the second space means "indistinct"; so, −) or +) may also indicate a C element. Such minor separations are caused by fixed barriers in the MODEL program.

P, product(s); P1, other product(s).

[a] B_0 is varied here.

E_2, is higher than that of the other step, E_1, from the reverse case ($E_2 < E_1$) where the symbol * is appended.

Hence, the complete model list consists of $20 \times 2 = 40$ two-step models (TRMs). For the model-determining program, the models G1AB and G2AB (identical with G12 and G22) and some of the "reverse" types (when the codes show only minor or no differences to the "normal" codes) have been neglected. In addition, the normal one-step models (types 1, 2 and AB) and some special models occurring in practice are added:
bimolecular autocatalysis 1A, A + B = B + B (+product(s));
normal catalysis KAT, A + B = product(s) + B;
the formal third-order reaction 3, A + A + A = product(s); and
the model PBA1 which differs from PAB1 or P1AB because, in contrast to all other models, the reference order is not assigned to reactant A (which by definition undergoes the parallel uni- and bimolecular reaction and is usually varied), but to the other, newly varied reactant, B.

Table 1 shows some of the MCC's of the remaining 32 models. These were obtained from theoretical series of files of rate curves, generated by numerical integration (program METEX, refs. 4, 12 and 14 and papers cited therein). The activation data of the two processes were $E_1 = 65$ kJ mol^{-1}, $k_{\infty 1} = 10^{12}$ min^{-1} or dm^3 mol^{-1} min^{-1} (standard reference reaction) and, in most cases, $E_2 = 87.4$ kJ mol^{-1} or 96.1 kJ mol^{-1} and $k_{\infty 2} = 17$ or 18, respectively, or $E_2 = 35$ kJ mol^{-1}, $k_{\infty 2} = 6$ for the reverse model type (index *), whereas the λ parameters (signal parameters) were $\lambda_1 = 10$ and $\lambda_2 = 5$, 15 or $-\lambda_1$ (G types).

For a fixed model, the influence of the activation parameters or even the signal parameters, λ, on the resulting code strings seems to be small, provided that extreme changes in the ratios λ_1/λ_2 are avoided [12,14]. Many of the MCC's are mentioned in ref. 14; a provisory, complete list can be obtained from the author.

COMPARING EXPERIMENTAL CODES—PROBLEMS AND SOLUTIONS

Finding the optimum two-step model (2R algorithm)

The strategy is to compare the experimental matrix with the theoretical matrix space by space, primarily restricted to the overlapping intervals (Fig. 2). Identical symbols give a match factor $w = 1$ (100% validity), whereas the greatest disagreement (i.e. + versus −) gives $w = 0$. Between these limits, different valuating scales were tested, see Table 2. It has proved advantageous to differentiate between uncertain values where a closing ")" is appended, and, for constancy, between "identity" (e.g. H versus H), $w = 1$, and "constant, but no identity" (e.g. H versus 1, M, etc.), $w = 0.5$. For standardization, such match factors are summed for all respective intervals,

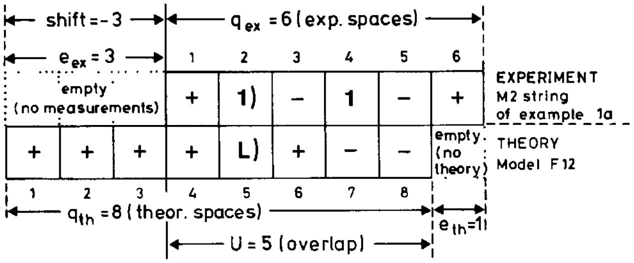

Fig. 2. Comparison of an experimental code with a theoretical code (M20 string).

and then divided by 3, i.e. referred to one mechanistic coordinate (rating sum B).

However, even in the case of equal string lengths of experimental and theoretical codes, it is difficult to generate a hit list of all TRM's based on the probabilities (0–100%). It would be unrealistic to assume that both strings can be compared without a certain shift of one, two or even more spaces against each other (Fig. 2) because this suggests that the same total concentration range and activation parameters which were set up for the rather arbitrary model simulations are being realized. In other words, the valuating algorithm has to be based both on a main optimizing quantity, the

TABLE 2

Different rating matrices

1) Simplest concept

	C^a	+	−)
C^a	1	0	0
+	0	1	0
−	0	0	1

2) Refined concept [4]; further elaboration

	C^a	+	+)	−	−)
C^a	1^b	0.50	0.75	0.50	0.75
+	0.50	1	0.75	0	0.50
+)	0.75	0.75	1	0.50	0.25
−	0.50	0	0.50	1	0.75
−)	0.75	0.50	0.25	0.75	1

3) Used in this article

	C^a	+	+)	−	−)
C^a	1^b	0	0.5	0	0.5
+	0	1	1	0	0
+)	0.5	1	1	0	0
−	0	0	0	1	1
−)	0.5	0	0	1	1

Column, experimental element; row, theoretical element; or vice versa.

[a] If) added, same value.

[b] Different orders, 0.75.

TRM, and on the shift. A negative shift means that $c(\min)$ of the theoretical model is lower than in the experiments, and vice versa. Thus, one is confronted with the problems of half-order [17,18] and comparability. To consider the effect of incomplete overlapping between experimental and theoretical codes (Fig. 2), different algorithms were studied which normalize the rating sums B with respect to the experimental string length, q_{ex}, the theoretical string length, q_{th}, and the following other characteristic lengths: the number of overlapping intervals (spaces), u; and the number of empty (non-corresponding) spaces, e_{th} and e_{ex}.

The following formula defines an evidence value of a model (compare ref. 11) by linearly relating the occupied spaces inside the experimental string (elements) to the union of the string elements, involving both the overlapping and the non-overlapping (empty) spaces

$$p_N = \frac{B}{u}\frac{u}{q_{ex}+e_{ex}} = \frac{B}{q_{ex}+q_{th}-u} \tag{1}$$

p_N can be seen as a probability which reaches a maximum for the case where all elements of the experimental string are identical with the elements of the model string; then a value of 1 (certainty) is obtained. In the other case, the real probability must be higher than p_N in eqn. (1) as the chance for agreement between an empty space of the theoretical string and an occupied space of the experimental string (or the reverse case) was assumed as zero whereas in reality it must be positive, but less than unity. This effect has been neglected as it would raise the probabilities only by 0–5%.

For validity of any TRM, the empty intervals of the theoretical string can be complemented (filled) by either its first or last element, respectively. In this case, these elements represent asymptotic limits, corresponding to kinetic limit cases for low or high concentration. For such a prolonged theoretical string, the probability is referred to B_F (the rating sum for the filling procedure), and the denominator, compared with eqn. (1), right fraction, is increased by substitution of u by q_{ex}. However, u has also to be used in the numerator, in order to consider the empty intervals of the experimental string

$$p_F = \frac{B_F}{q_{ex}}\frac{u}{q_{ex}+q_{th}-q_{ex}} = \frac{B_F u}{q_{ex}q_{th}} \tag{2}$$

Comparison of fill and non-fill probabilities (eqn. (1) and (2)) yields a further criterion as to whether or not a definite TRM may be useful. In the first case, it is necessary (but not sufficient) that

$$\frac{p_F}{p_N} = \frac{B_F}{B}\frac{u}{q_{ex}} > 1 \tag{3}$$

Testing a combination of two-reaction models (4R algorithm)

More complex models may be recognized after fragmentation of the total concentration range into several domains, each representative of one TRM. For simplicity, this problem may be restricted to a superposition of two models. It seems evident that the resulting probability for a four-reaction model (FRM) is obtained from the particular probabilities, p_1 and p_2, as a weighted average

$$p = \frac{u_1 p_2 + u_2 p_2}{q_{\min}} F_1 \tag{4}$$

where u_1 and u_2 are the numbers of the overlapping spaces between experimental string and both theoretical strings, $q_{\min}$ is the minimum of q_{ex} and $(u_1 + u_2)$, and F_1 is a special correction factor describing the additional information change caused by the interaction of both theoretical strings

$$F_1 = \frac{u_1 + u_2 - 2(x_- n_g + x_+ n_d)}{u_1 + u_2} \tag{4a}$$

A loss (factor x_-) results if there are n_g blanks (gaps) between these strings, whereas a gain (factor x_+) stems from n_d overlapping spaces, causing double information. The factor x_- should be zero for the use of eqn. (4) because the loss is already considered in the probabilities p_1 and p_2, whereas the choice of x_+ is a philosophical problem. For the limiting case of selecting two identical, correct and unshifted model strings (i.e. $p_1 = p_2 = 1$), a probability of 1 should result; thus, $x_+ = 0.5$ should be correct. However, if the second mechanism is a submechanism of the first, there should be a certain resonance effect which should increase the overall evidence values in order to indicate that the approach is correct, i.e. a lower value than 0.5 should be assumed for x_+. For the later calculations, we use $x_- = 0$ and $x_+ = 0.3$. The case of two identical TRMs is avoided by the requirement of a minimum shift of 2 blanks between both theoretical strings.

An alternative algorithm was tested which is directly based on the rating sums B_1 and B_2, using

$$p_{\mathrm{D}} = \frac{B_1 + B_2}{q_{\mathrm{ex}} + e_{\mathrm{th}_1} + e_{\mathrm{th}_2}} F_1 \tag{5}$$

in which the paramount difference from eqn. (4) is that the sum of $B_1 + B_2$ is referred to the number of experimental spaces, not of overlapping spaces, and the empty spaces appear explicitly in the denominator, but not in the particular probabilities.

RESULTS AND DISCUSSION

Our experience with the new fingerprint method is based on one hundred experimental concentration series involving very different reactions in solu-

TABLE 3

Results of reaction analysis

No./method Expts/q_{ex}	Initial concs. (M) Reactants/solvent	Best TRM [a] P_F/P_N [b] (%)	Best FRM [ac] (%) eqn.	Comparison with literature [d]
1a/DTA 9/6	0.002–0.0028 $Ce(SO_4)_2$ +0.025 MA in 1.25 H_2SO_4	GAB1/G12/KAT 41.7/41.7	G12+AB 56.4 5 F1AB+G21 53.3 5	Prereactive equilibrium. Repeated reaction of Ce^{4+} with oxidized reactant. Consecutive process involving intermediates.
1b/UV 11/7	$(5–50)\times10^{-5}$ $Ce(SO_4)_2$ +0.00375 MA in 1.25 H_2SO_4	3 51.7/47.6	P2A+G12 57.7 4 P21+3 62.2 5	Prereactive equilibrium. Recoupling as for 1a. Parallel mixed-order branches. Formal third-order process caused by repeated reaction with oxidation products formed.
1c/UV 14/8	2.5×10^{-4} $Ce(SO_4)_2$ +0.0013–0.0038 MA in 1.25 H_2SO_4	1A 54.2/54.2 (GAB1 : 48/41.7)	P2A+1A 43.0 5 Fragmentations unattractive	LC: Recoupling as for 1a, but to a smaller degree. HC: Chain character because organic radicals formed.
2/DTA 15/8	0.01–0.0125 $NaBrO_3$ $+2.5\times10^{-4}$ $Ce(SO_4)_2$ + 0.375 MA in 1.25 H_2SO_4	P2A* 52.1/35.4 (P21 : 43.8)	PBA1+P2A* 46.9 4	Splitting into reaction branches and recoupling facilities of intermediates, typical for the known FKN mechanism [4].
3a/DTA 15/7	0.05–0.8 Aniline +0.22 $NaNO_2$ in 2.5 H_2SO_4	PAβ1* 54.2/54.2	Fragmentations not attractive	Distortions of the first-order denitrogenation by coupling reaction and/or dehydration.
3b/DTA 16/7	0.02–0.8 Aniline +$NaNo_2$ (1:1) in 2.5 H_2SO_4	P21 53.8/47.6	G12* +AB 50.7 5	LC: Equimol. fragments of the diazotization give rise to a "reverse" reaction. HC: Denitrogenation suppressed by bimolecular processes (with remaining product?).

4/DTA 10/6	0.02–0.13 *p*-Dimethyl-phenylin-isoxalidin in *o*-xylene	P21 52.8/52.8	G12 * + P21 $\underline{55.6}$ 5	Fragmentation of the compound followed by partial regeneration (re-aggregation [21]).
5/DTA 10/6	0.2–0.5 2-cyclooctenone + 1.04 CHD in methylcyclohexane	F2AB 50.0/50.0	FAB1 + AB $\underline{53.3}$ 5	LC: Secondary reaction. HC: Diels–Alder reaction occurs [27].
6/DTA 6/5	0.12–0.52 PhCSOCPh in Ph_2CH_2 (oxygen atmosphere)	F1AB 46.7/46.7	F12 + F1AB ($\underline{57.5}$) 4 or 5 Strongly related	The oxidation is followed by dimerization. HC: The latter accompanied by further processes [22]
7/DTA 8/7	0.02–0.36 $(PhO)_3PO_3$ in CH_2Cl_2	1A 39.6/39.6 Small contribution	P1AB + P1A 43.3 5	LC: Contamination of the ozonide by unreacted phosphite. HC: Recoupling of decomposition product formed with reactant [26].
8/DTA 11/7	0.0001–0.29 1-methyl-butene(− 2) + 0.3 $(PhO)_3PO_3$ (formed in situ) in CH_2Cl_2	PAB1 57.2/47.6 PBA1 50.0 1A $\underline{54.2}$	Fragmentations unattractive	Parallel decomposition of ozonide and bimolecular reaction of the butene. Autocatalytic process based on by re-formation of ozonide [26].
9/DTA 13/8	0.0006–0.63 NMFA-endoperoxide (formed by photoxygenation) in methanol	P2A 44.6/38.9	P1AB + P2A $\underline{54.5}$ 5	Parallel decomposition, addition of methanol and dimerization. HC: Recoupling of hydroperoxide with reactant [25].
10/DTA 16/7	0.005–0.025 I_2 + 0.78 H_2O_2 in H_2O	AB 66.7/40.5 (GAB1 : 52.4)	F21 + GAB1 $\underline{58.9}$ 5	LC: Pseudo-unimol. decomposition of HIO. HC: Second-order reaction between I_2 and H^+ (after fast predissociation [23,24]).

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[a] The best utility value of the 2R and 4R algorithm is underlined (non-filling mode).

[b] Utilities using the filling and non-filling algorithm.

[c] Only non-trivial (unrelated) combinations are considered.

[d] The next-best candidates of the model list (cf. Tables 5 and 6) cannot be discussed in this concentrated survey. LC: Conditions at low initial concentration, HC: conditions at high concentration.

Other abbreviations: CHD = Cyclohexadiene (− 1.3); MA = Malonic acid; NMFA = N-methyl-furfurylamin; Ph = phenyl.

TABLE 4

Mechanistic concentration codes of the examples given in Table 3

No. 1a	1	+	−	L1	+	M			No. 1b	H	H	H	−	+	−	M	
	+	1)	−	1	−	+				+	−	H	H	H	+	+)	
	+	+	−	2	−	−				2	−	2	H	+	2	2	
No. 1c	−)	+	−)	1	+	1	1	M	No. 2	M	−	L	+	L	−	1	1)
	−	H	−)	+	−)	+	−	−		−	+	+	−	H)	2	2	2
	−	2	−)	+	−)	+	L	−		−	M)	M	M	M	1	M	1
No. 3a	+	L	+	1L	1	1	+		No. 3b	L1	+)	1	+	−	+	M	
	1	+)	−)	1	1	1)	+)			−	1	+	L	L	−	M	
	M	+	−	M	M	M)	+			2	2	+	−	2	−	+	
No. 4	1	L	+	2	2	−			No. 5	+	+	−	−	+	−		
	+)	+	−	+	1	−				+	M	−	−	−	+		
	1	+	−	L	L	1				1L	+	−	1	1	+		
No. 6	−	+	M	−	1L				No. 7	+)	−	+	−	M	+	−	
	+	1	+	−	+					L	−	M	+	−	−	+	
	1L	1L	+	−	+					−	+	−	+	L	L	−	
No. 8	M	M1	−)	+	−	1)	1		No. 9	+	+	+	−	2)	+	1)	−
	2	+	−)	+	−	+	M2			−	1	+	+	−	2)	H)	+
	1	1	−	M	−	+	−			2)	+	M)	2	2)	H	H)	+
No. 10	+	+)	1)	1	−)	+)											
	−	2	+)	−)	1	−											
	1M	1M	+	1)	−	M)											

TABLE 5

The best two-reaction models for the oxidation of malonic acid by ceric sulphate

Pos.	Model	Length	Shift	n_{end} *	Utility (%)	
					Unfilled	Filled
1	KAT	6	0	0	41.7	41.7
	GAB1	6	0	0	41.7	41.7
	G12 *	5	0	−1	41.7	41.7
2	P1A *	6	0	0	40.6	40.6
3	G12	5	−1	−1	40.5	38.9
4	F1AB	5	−1	−2	38.1	35.6
5	FAB1	6	0	0	36.1	36.1
	P1AB	4	+1	0	36.1	41.7
6	F2AB	7	0	+1	35.7	35.7
7	P12 *	8	−2	0	35.4	35.4
8	P1A	7	−1	0	34.7	34.7
9	F21	9	−2	+1	33.3	33.3
10	1A	8	0	+2	31.3	< 33.3

Example 1a in Tables 3 and 4; $[\mathrm{Ce(SO_4)_2}]_0$ was varied. The experimental MCC shows 6 intervals. The fill-mode is unfavourable here (class 3).

* indicates excess of theoretical elements at the end of experimental string.

tion [2,13], which have also been studied by other groups using conventional methods, so that the various reaction mechanisms have been established.

Representation of a special example

The complex reaction between ceric sulphate and malonic acid [19] is related to the best studied chemical oscillating reaction, the Belousov–Zhabotinsky reaction of bromate, redox salt and malonic acid in 1.25 M aq. sulphuric acid [4]. Nine DTA experiments [20] were performed for varying inputs of $\mathrm{Ce(SO_4)_4}$ (0.002–0.028 M) and 0.0025 M malonic acid (example 1a in Table 3). The initial temperatures were 258–280 K for a heating rate of 1.5 K min^{-1}. The resulting MCC is listed in Table 4, the M20 index string is also shown in Fig. 2, and the best models using the 2R algorithm are presented in Table 5, both for fill and non-fill mode.

This very complex reaction is a crucial example, as the reproducibilities of the parameters are poor because of their extreme sensitivity towards small concentration changes and the presence of oxygen. The best two-reaction models, KAT ($A + K = B + K$), GAB1 and G12*, show only a probability of 41.7%. However, supposing a combination of two TRMs, i.e. using the 4R algorithm, one obtains, on the basis of eqn. (4), the best FRMs of G12 + P1AB (45.7%), GAB1 + AB (45.3%, but trivial case), or KAT + AB (45.3%); on using eqn. (5), G12 + AB (56.4%; Table 6). The last probability is much

TABLE 6

The best three-or four-reaction models for the same series

First model/shift (low conc.)	Utility (%)	Second model/shift (high conc.)	Utility (%)	Total utility	n_g [a]	n_{end} [b]
Eqns. (1) and (4)						
G12/−1	40.5	P1AB/+1	41.7	45.7	+3	0
GAB1/0	41.7	AB/+3	30.0	45.3	+3	+1
KAT/0	41.7	AB/+3	30.0	45.3	+3	+1
F1A/−1	38.1	P1AB/+1	41.7	44.4	+3	0
Eqns. (1) and (5)						
G12/−1	40.5	AB/+3	30.0	56.4	+1	+1
		G21/+3	36.1	55.2	+1	+1
F1AB/−1	38.1	AB/+3	30.0	54.2	+1	+1
		G21/+3	36.1	53.3	+1	+1
G12/−1	40.5	P12/+3	< 35.4	46.7	+1	+2

Example 1a, see Tables 3, 4 and 5; FRM approach much better than TRM approach.

[a] Spaces overlapped by both theoretical strings.

[b] Excess of elements of the second model at the end of the experimental string.

higher than those for the TRMs, but does not seem high enough to consider this to be a satisfactory assumption.

Nevertheless, the best models listed in Table 5 represent parts of the total mechanism, as discussed in the literature [19,20].

1. KAT: quasi-catalytic function of cerium ion, because this is partially retained after the oxidation reactions with malonic acid of their oxidation products (tartronic acid, glyoxylic acid) or organic radicals.
2. P1A*: tartronic acid, the first stable oxidation product, is oxidized by the reference reactant, $Ce(SO_4)_2$.
3. GAB1: before the first oxidation, a complex is reversibly formed from the reactants.
4. G12, G21: because malonic acid is in strong excess in most experiments, the GAB1 type may be approximated by the related models G12 and G21. This problem needs further investigation.
5. AB: the normal bimolecular reaction between the reactants.
6. P1AB: indicates a certain discrimination into the main reaction (strong excess of malonic acid, index 1) and the direct bimolecular process (index AB).

The result of the reaction–analytical approach is independent of the method. This is stressed by the results of the UV series of the same reaction (ceric sulphate varied, example 1b of Table 3). Here, the excess of malonic acid is much smaller and as a consequence, steps of molecularity 2 are preferred. The overall picture, however, including this restriction, is scarcely different from that of the other series (examples 1a, c).

1. KAT: no indications since the reactant concentrations of A and B are rather similar.
2. P1A*: substituted for by P2A.
3. GAB1: rather G21 or G12 (*).
4. G12: as expected.
5. AB: less preferred.
6. P1AB: substituted for by PAB1 (i.e. bimolecular step preferred) or by FAB2 (secondary oxidation products may react at higher temperature, causing signal splitting).

Results and discussion of other series

The results of the 13 examples of series in Table 3 [21–27] confirm that the new approach is promising for the following reasons: (1) the best models are compatible with the known results, given in the last column; (2) related systems yield related codes and models (e.g. examples 1a–c, 2, 3a,b); and (3) a distinct correlation between the "complexity" of the system and the results is obtained (see Table 7).

The averages of four variables, namely the two probabilities of the best TRM and FRM approach, the "fill" factors $F_2 = p_F/p_N$ in eqn. (3) and the "selectivity" factors F_3 defined by the ratio of the percentages of the best model over the next best not-related model (e.g., G12 and G21, FAB1 and F2AB are related), reveal typical trends if they are assigned to four classes of increasing complexity (see Table 7). The evidence values of both approaches appear in the expected classes of strong preference; TRM percentage and fill factor are decreasing with enhanced distance from class 1, whereas the selectivity passes a maximum in class 2. This irregularity may be caused by

TABLE 7

Trends in variables assigned to classes of increasing complexity

Class	Description	Evidence value of			
		best TRM	best FRM	F_2	F_3
1	Strong preference of a particular TRM (examples 3a, 8 and 10)	51.0	ca. 38	1.28	1.18
2	Difficult decision on better utility of TRM or FRM approach (examples 2, 3b, 5)	47.1	50.3	1.16	1.25
3	Strong preference of a particular FRM (examples 1a, 1b, 4, 6, and 9)	45.6	53.4	1.05	1.14
4	Neither TRM nor FRM approach seems attractive; system too complex (example 7)	39.6	43.3	1.00	1.10

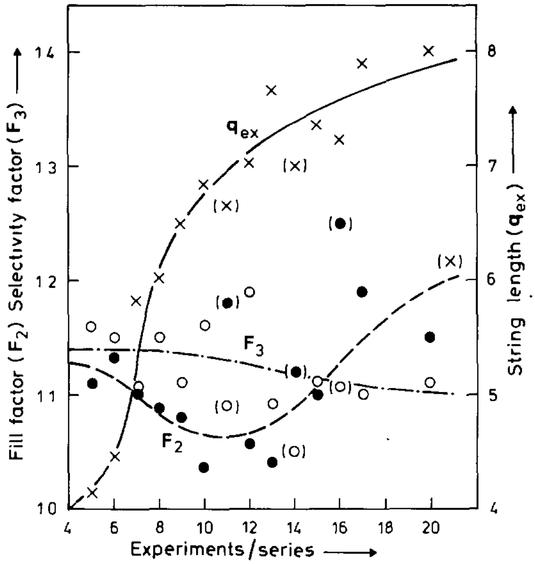

Fig. 3. Number of experiments, string lengths, and fill and selectivity factors: ×, string length (number of code intervals); o, selectivity factor; and ●, fill factor. Points in parentheses are neglected because statistically insignificant (1–2 particular values only).

the small number of examples. Therefore, the results of all series were subjected to a more detailed examination.

General discussion of all series studied

The required string length should depend on both the complexity of the kinetics, expressed by the number of C elements, and possibly on the number of experiments per series, since this has to exceed the string length considerably. A MCC string can be confirmed by its invariancy when more experiments are performed inside the concentration gaps (compare Fig. 1). Most of the systems studied have not been subjected to such a test, because the primary intention was to get a simplified, preliminary view, not exhaustive information.

Indeed, the string length increases with the number of experiments per series (Fig. 3): slowly, at first, then, for 6–8 experiments, very steeply. But with more experiments, the increase slows down and possibly becomes asymptotic; from the slope one may estimate that more than 10 further experiments in a series are needed to yield one additional string element! Hence, it should become difficult to identify processes involving 6 or more steps even if many more than 20 experiments were performed.

The selectivity factor, nearly constant for 4–6 experiments, later shows a steady decrease, as the range for a good TRM fit is left when many more experiments had to be planned; the string lengths for the TRMs are 4–9 (Table 1; average 5.91).

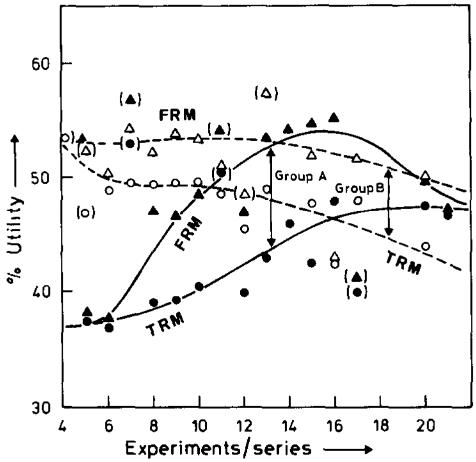

Fig. 4. Comparison of TRM and FRM fits for different numbers of experiments per series: group A, max. % (filled) > max. % (unfilled); and group B, max. % (filled) ≤ max. % (unfilled). Group A: ●, TRM fit; and ▲, FRM fit. Group B: ○, TRM fit; and △, FRM fit. All points correspond to average values. Points in parentheses are neglected because statistically unsignificant (1–2 particular values only).

The fill factor reveals a first maximum for 4–6 experiments per series, but for more than 13 experiments there is a second maximum which is difficult to understand. For those series where the fill procedure improves the fit (Group A, 41 series, Fig. 4), the evidence value for a TRM approach increases to a maximum (14–17 experiments/7–8 spaces), yielding, on average, 47% (filled 57%) probability. However, the FRT models already

TABLE 8

Statistical results for four classes of complexity

Class	Number of series	Average values					Ratio of utilities FRM/TRM approach
		Experiments/ series	String length	TRM approach			
				Maximum utility [a]	Fill factor	Selectivity factor	
1	10	9.50	5.80	54.0	1.45	1.15	1.00
2	26	9.13	6.20	48.8	1.04	1.16	1.04
2/3	18	10.50	6.17	48.1	1.13	1.14	1.06
3	42	11.31	6.71	46.6	1.13	1.11	1.20
4	7	9.29	5.86	37.9	1.66(?)	1.12	1.02

[a] Non-filling percentage, eqn. (1).

From class 1–4, the complexity of the systems is increasing, indicated by the steady decrease of the utility, of the selectivity and, partially, of the filling factor of a two-reaction approach. Class 1 represents the cases for the best two-reaction approach while for class 3, the four-reaction approach is the best.

The results of class 4 are statistically less significant. (The row "class 2/3" implies that the decision on the better type of approach is difficult.)

show a better fit for series with 8 experiments. Conversely, in the B group (54 series where filling gives no improvement, Fig. 4), the TRM and FRM probabilities, first nearly constant (50% and 53%), continuously decrease for more than 10 experiments. In conclusion, the 2R algorithm shows the best success for less than 10 experiments/series for group B, but in general the 4R algorithm is better for both groups; however, for more than 13 experiments (16 for group A) even FRM fits become less and less promising. Consequently, such series involve more complicated mechanisms, with 5 or more effective steps.

Refined classification of all series, reveals an increase in the number of experiments performed, in the string length (to a minor degree) and in the superiority of the FRM approach with increasing complexity (Table 8). However, the very low fill factor of only one example (No. 7) was obviously not representative for the most complex class, 4, as the average value for the seven series is much higher. Therefore, a high fill factor is only a sufficient prerequisite for assuming a TRM if a high probability is assigned.

CONCLUSION AND OUTLOOK

It has been demonstrated that the program MODEL can be applied to thermoanalytical measuring curves, yielding a list of the best kinetic models (containing 1–4 steps) in the order of percentages which could be interpreted as probabilities (Tables 5 and 6).

The highest value was 63.9% (unfilled) for a TRM approach, even 68.8% for a FRM approach. Such percentages seem rather low for a good fit if compared with quantities such as the confidence level or the correlation coefficient, but for this type of quantity an approach to 100% is generally impossible. Such a demand would require equal lengths of theoretical and experimental strings, identity of all elements and absence of any concentration shift, experimental error and inaccuracies in the computer calculations. The conditions for experiments and simulations cannot be identical in all details, as was discussed for the starting concentration. Furthermore, the orders involved in the C elements are slightly modified by the signal parameters (as enthalpies for DTA) of the particular steps, and, to a minor degree, by the activation energies. A general mathematical proof for their desirable independence cannot as yet be given, although all recent studies imply that in non-isothermal kinetics a 'theorem of common kinetic runs' exists for every model, which is expressed by the existence of the MCCs [12,14].

Hence, the percentages presented should be seen rather as relative quantities, utilities or evidence values [11]. However, the best candidate in the list of less and less probable models must not always be sufficient to describe the kinetics in detail. For rather complicated mechanisms, these evidence values represent merely the contributions of the submechanisms involved. This dissection problem will be discussed in a forthcoming article where thermoanalytical curves based on a multi-step mechanism, constructed by successive expansion of an elementary reaction, are analysed using the MODEL program.

In conclusion, the combination of appropriate equipment (as described in refs. 2, 13 and 28) with the new evaluation principles represents a "kinetic receptor" for the chemist, which enables him to also systematically analyse the kinetics of less known systems (cf. [4,14]). For a system with *n* components, a routine calculation of the *n* mechanistic matrices is possible which represents a practice-based alternative to the basic ODE matrix [16,29] as the obligatory description of every homogeneous reaction mechanism. Therefore, an unambiguous kinetic characterization can be reached [2], at least for the field of mass action kinetics, and the strategy can also be transferred to fast reaction kinetics (cf. ref. 30), or to conventional isothermal reaction kinetics [7].

Of course, there is still a long way to go towards adapting commercial instruments to the needs of calculating standardized activation data, half-widths, and shape indices, towards confirming the general validity of the new global kinetic theorem, from the point of view of the different methods and towards refining the calculations, in order to obtain absolute probabilities.

Another aspect is to elaborate the mechanistic matrices of heterogeneous models. An important prerequisite would be to formulate an obligatory list for all basic heterogeneous mechanisms [13,31]. But a severe problem is that the applicability of the principle of resolving complicated models into elementary steps, an extremely successful strategy in homogeneous reaction kinetics, seems to be questionable in solid state studies [6,32]. However, based on experiences with the reduced-time method [33], the influence of the heating rate could be utilized for developing an analogous procedure.

After the installation of appropriate data banks of reaction mechanisms for other transmitter parameters such as the heating rate, kinetic curves can be interpreted more systematically, which is important in a period where the capability of "interdisciplinary network thinking" is not as widespread as should be desirable.

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