

STUDY OF BIMOLECULAR REACTIONS IN SOLUTION BY NON-ISOTHERMAL METHODS*

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ABSTRACT

The undistorted progress of bimolecular processes in solution can be studied by DTA experiments followed by the estimation of shape index and half-width and the reference of these quantities to the corresponding rate curves.

Empirical relationships are presented which we derived by digital computer application and which allow calculation of the above corrected values for reactions with or without equimolecular ratio of the reactants. The application is illustrated by the evaluation of DTA curves of some reduction, oxidation and Diels-Adler reactions. Additional computer-generated DTA curves based on the evaluated activation data and reaction enthalpies confirm the results.

The significance of the order in non-isothermal reaction kinetics, referred to time, is discussed.

1. INTRODUCTION

Undoubtedly, a simple method of controlling the "undistorted" progress of bimolecular reactions in solution would save many unsuccessful preparative experiments in chemical synthesis. Thus, for any reaction, it is of great interest to know the most efficient ratio of the reactants or the most suitable reaction temperature.

For these reasons, we have considered using non-isothermal methods, especially DTA¹. Starting with a first-order reaction at a constant heating rate, we have shown² that the shape index and the activation data extracted from a DTA curve can be used to calculate two parameters which define the type of reaction on which the corresponding non-isothermal rate curve is based, viz. the corrected shape index and the reaction type index. However, for second-order reactions the relationships presented are not applicable.

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The aims of this paper are to derive adequate expressions for bimolecular reactions based on Koch's approximate kinetic theory³ and to test them by the use of various examples of reactions in solution.

II. BASIC THEORY

Considering the DTA curve of a first-order reaction in stirred solution¹, half-width and shape index may be transferred to ideal kinetic conditions, i.e. rate curve instead of DTA curve involving maximum temperature difference² $\Theta_m \rightarrow 0$, by the use of the empirical formulae

$$h_{x1} = \frac{n + [h - (m \ln 2/c)] [a_3 + a_5 \ln(uc)] (\Theta_m/u)}{1 + \{a_1/[(u + a_2)uc]\}} \quad (1)$$

and

$$S_{x1} = \frac{(uc)^{b_1} S}{[(uc)^{b_1} + b_2] [1 + (b_3 + b_6 uc)] (\Theta_m/u)} \quad (2)$$

where h = experimental half-width, h_{x1} = half-width of the corresponding rate curve, S = experimental shape index, S_{x1} = shape index of the corresponding rate curve, m = heating rate (K/min), c = cell constant (min^{-1}), Θ_m = maximum temperature difference, $a_1, a_2, a_3, a_5, b_1, b_2, b_3, b_6$ = constants given in ref. 2.

The parameter $u (= u_m)$ is obtained by the substitution

$$\int_0^t k(t) dt = u(t) k(t)$$

which yields the approximation

$$u(t) = \frac{RT^2}{mE} = \frac{E}{Rm [\ln k_x - \ln \hat{k}(t)]^2} \quad (3)$$

where R = gas constant, E = activation energy (kJ/mole), k_x = frequency factor (min^{-1} or $\text{lmol}^{-1} \text{min}^{-1}$). To express $u(t)$ by the half-width in the case of a first-order reaction, $\hat{k}(t)$ has to be taken at the maximum on the rate curve².

$$\hat{k}(t) = k_m = \frac{1}{u_m} = \frac{1}{u(tm)} = \frac{1}{u} \quad (4)$$

For a second-order reaction



it was derived and confirmed³ that

$$\hat{k}(t) = \frac{1}{2[A]_0 u_m} = \frac{k_m \text{ (first order)}}{2[A]_0} \quad (5)$$

When we consider a bimolecular reaction of the type



k_m must depend on the initial concentrations of both reactants. Then, one may assume that an expression analogous to eqn. (5) for $k(t)$ in eqn. (3) is valid, i.e.

$$\hat{k}(t) = \frac{1}{u_m d [A]_0^a [B]_0^b} \quad (6)$$

where $d = \text{constant}$.

For the estimation of d , a , and b , the half-width and the theoretical reaction type index may be used; the latter is defined as

$$M = \frac{R m u}{(\log e)^2 h_{ideal}} = \frac{R}{(\log e)^2 \ln(k_2/k_1)} \quad (7)$$

where k_2/k_1 represents the ratio of the rate constants at the first and second half-width point of the curve. For the first limiting case, the pseudo-unimolecular first-order reaction (large excess of reactant), $M_1 = 0.020 \text{ kJ/mole K}$, while for the second limiting case, the second-order reaction, $M_2 = 0.013 \text{ kJ/mole K}$ is valid. The latter theoretical value allows us to fit eqn. (6) by evaluating theoretical DTA curves of the AB-type (see Sect. V).

The parameter u , defined by eqn. (3) for the rate constant $\hat{k}(t)$, could be denoted as "specific time" since, for unit heating rate, m , and unit rate constant, this value generally is the fraction $1/\ln(k_2/k_1)$ of the half-width of the rate curve, i.e. $h/2.25$ for a first-order and $h/3.5$ for a second-order reaction ($[A]_0$ is assumed to be unity).

III. COMPUTER APPLICATION

Using the digital computer PDP 10 system in Mülheim/Ruhr⁴ (Digital Equipment Corp., Mass., U.S.A.), we developed two different kinds of program.

In order to simulate theoretical DTA or rate curves, we used FORTRAN IV programs based on repeated integration of the kinetic differential equations including the derivatives up to order 4 in a Taylor expansion. Two to ten products related by any reaction may be assumed; control of the accuracy was performed by examining the constancy of the sum of all concentrations after every step and, if necessary, reducing the instantaneous value of the time interval. The resulting curve was projected on a DEC VT 55 terminal with copier; in addition, all important curve data were recalled in alphanumerical mode.

By various repetitive routines, experimental curves can be fitted rapidly by a change of the prevailing activation data (directly or by only varying the width of the curve) and/or the weight of any step.

A second family of programs served for evaluation and was based on the following kinetic equation⁵.

Unimolecular process (first order)

$$k = \frac{c(T)\theta + \dot{\theta}}{c_p(T) \int_0^t \theta dt - \theta} \quad (8)$$

Bimolecular process (second order if $[A]_0 = [B]_0$)

$$k = \frac{V\Delta H}{C_p(T)} \frac{c\theta + \dot{\theta}}{\left(c \int_0^t \theta dt - \theta \right) \left\{ ([B]_0 - [A]_0) \frac{V\Delta H}{C_p} + c \int_0^t \theta dt - \theta \right\}} \quad (9)$$

where $T = mt + \theta_m^*$. The temperature dependence of the heat capacity, C_p , may be neglected in most cases.

After input of up to 100 points of the curve, the initial concentrations of the reactants and 5 parameters which describe the temperature-dependent cell constant and heat capacity (recalled by solvent key numbers), the rate constants are calculated for equidistant time intervals. Using the least square method for fitting $\ln k$ vs. $1/T$ by a straight line, four sets of kinetic data (activation energy, frequency factor, correlation coefficient, specific time and specific temperature) were calculated for the initial part (25% of the curve) and the total curve as well as an assumed unimolecular or a bimolecular initiating reaction, respectively. Hence, the computer performed a double interpretation, based either on the initial data or on the overall data. The initial order was selected by the experimenter: only the orders 1 (unimolecular inducing step) or 2 (bimolecular inducing step) were possible. Wrong selection could be corrected after study of the results. In the case of the overall order, the program took that order which corresponded to the best correlation coefficient and then presented the most probably basic type of mechanism.

IV. CORRECTION OF HALF-WIDTH AND SHAPE INDEX FOR A SECOND-ORDER REACTION

The path which we used for finding empirical expressions for S_{idc1} and h_{idc1} from both experimental quantities was analogous to the first-order case. We generated theoretical DTA curves for unit initial concentration, heating rate 1.5, the cell constants 0.05, 0.08, 0.12, 0.14, 0.18, 0.25, 0.50 min^{-1} (= const.) and the 20 test reactions mentioned in ref. 2 which corresponded to u_m values between 0.46 (reaction 1) and 33.33 (reaction 20). The study of the half-widths obtained in this way shows that, using the expression for no temperature feedback,

$$h_{*2} = \frac{(uc)^{1.1}}{(uc)^{1.1} + f(u)} = h_c \quad (10)$$

* This, however, is not an obligatory condition for the validity of eqns. (8) and (9).

TABLE I

DTA HALF-WIDTH FOR A SECOND-ORDER REACTION (TEMPERATURE-FEEDBACK INCLUDED)

Reaction No.	$\log k_x$	u_{xx}	$1.4(2.3 \pm u)a_1$	Deviation from mean value (%)
2	12	0.88	0.415	-19
3	15	1.63	0.233	-54.6
4	20	2.28	0.784	+52.7
6	15	3.88	0.762	-48.4
7	12	3.96	0.415	-19.10
9	20	5.78	0.590	+14.9
10	14	5.77	0.464	-9.6
12	7	8.05	0.595	+15.9
13	4	10.05	0.526	+2.4
14	12	11.08	0.478	-6.8
15	4	14.20	0.630	+22.6
16	10	15.10	0.576	+12.2
17	12	17.90	0.446	-13.2
19	5	23.2	0.545	+6.1
20	6	33.33	0.487	-5.2
Average			0.514 ± 0.038 (standard error)	

$f(u)$ is practically constant (though not for the analogous first-order equation):

$$f(u) = 0.19 \pm 0.01.$$

If the influence of the temperature difference signal becomes noticeable, h may be represented by the expression

$$h_{x2} = \frac{a_1 \Theta_m [h - (m/c) \ln 2] + h}{1 + 0.19 (uc)^{-1.1}} \quad (11)$$

where a_1 was found to be

$$a_1 = \frac{0.7}{2.3 + u} \quad (12)$$

Table I gives an idea of the deviations observed which increase when $\log k_x$ is not in the usual range of 5-15.

Similar results are obtained for the shape index. In the absence of additional heating by the reaction, the ideal shape index is

$$S_{x2} = \frac{(uc)^2}{(uc)^2 + b_1 u} S = S_c \quad (13)$$

where b_1 is only a function of u (Table 2).

$$b_1 = 0.0375 - 0.00138 u \quad (14)$$

TABLE 2

SHAPE INDEX FOR A SECOND-ORDER REACTION (NO TEMPERATURE FEEDBACK)

Reaction No.	u	$b_1 \times 10^2$		Reaction No.	u	$b_1 \times 10^2$	
		Computer	Eqn. (14)			Computer	Eqn. (14)
1	0.46	3.53	3.69	11	6.21	3.45	2.94
2	0.58	3.06	3.64	12	8.05	2.96	2.70
3	1.38	2.80	3.57	13	10.05	2.99	2.44
4	2.27	2.55	3.45	14	11.08	1.38	2.31
5	2.46	3.41	3.43	15	14.21	2.05	1.90
6	3.58	2.80	3.25	16	17.90	0.99	1.43
7	3.96	3.08	3.24	17	17.91	2.67	1.43
9	5.79	2.31	3.00	18	17.91	1.40	1.42
10	5.77	2.36	3.00	19	23.27	1.10	0.72
				20	33.33	2.67	-0.58

(Mean value: $b_1 = 0.0252 \pm 0.018$)

TABLE 3

FEEDBACK PARAMETER b_2 FOR THE CORRECTION OF THE SHAPE INDEX

Reaction No.	u	b_2		Eqn. (16)	b_2 [computer] b_2 [eqn. (16)]
		Computer	Eqn. (16)		
1	0.46	0.045	0.038	0.105	4.29
2	0.58	0.024	0.011	0.076	3.16
3	1.38	0.114	0.015	0.060	1.83
4	2.27	0.080	0.004	0.047	1.70
5	2.46	0.079	0.004	0.045	1.76
6	3.58	0.043	0.015	0.036	1.19
7	3.96	0.042	0.017	0.036	1.17
9	5.79	0.033	0.001	0.029	1.14
10	5.77	0.028	0.004	0.031	0.90
11	6.21	0.032	0.008	0.029	1.10
12	8.05	0.027	0.005	0.025	1.08
13	10.05	0.028	0.002	0.022	1.27
14	11.08	0.019	0.009	0.021	0.91
15	14.21	0.032	0.017	0.019	1.68
16	17.90	0.010	0.005	0.017	0.59
17	17.91	0.083	0.064	0.017	4.88
18	17.91	0.015	0.008	0.017	0.88
19	23.27	0.021	0.033	0.015	1.40
20	33.33	0.007	0.003	0.012	0.58

In order to consider heat feedback, we tested the simplified relationship analogous to eqn. (35) in ref. 2

$$S_{s,2} = (1 + b_2 \theta_m) S_c \quad (15)$$

by calculation of b_2 using different u , c , and θ_m values and $S_{s,2} = 1.15$. The value of

b_2 was found to be constant for any particular reaction and there was no remarkable influence of the cell constant, c . Involving other reactions, b_2 could be generally formulated as proportional to the inverse square root of u (Table 3)

$$b_2 \approx \frac{b_3}{\sqrt{u}} \quad (16)$$

incorporating $b_3 = 0.071$. This relationship shows satisfactory agreement when u values > 1 and < 16 are considered.

For all of the approximate formulae, the deviations for large u values are not serious since, then, the influence of the correction is generally small.

The correction formulae based on these empirical equations are given by

$$h_{x,2} = \frac{[h - (m/c) \ln 2] \{ [0.7/(2.3 + u)] \Theta_m \} + h}{1 + 0.19 (uc)^{-1.1}} \quad (17)$$

and

$$S_{x,2} = \frac{S}{1 + (0.071/\sqrt{u}) \Theta_m} \frac{(uc)^2}{(uc)^2 + (0.0375 - 0.00138 u)u} \quad (18)$$

They are valid for unit concentration and for not too strong heating effects ($\Theta_m < 10$ K) and, similarly to the first-order expression, depend only on the specific time, u , cell constant, c , and maximum temperature difference, Θ_m . The limiting cases are consistent with these equations. If c or u is increased, $h_{x,2}$ and $S_{x,2}$ approach the experimental values h and S , respectively; in the opposite case, $h_{x,2}$ tends towards the half-width of the simple heat-decay curve. However, for $u \rightarrow 0$ or $c \rightarrow 0$, the shape index disappears.

V. NON-EQUIMOLECULAR RATIO OF THE REACTANTS

For the study of bimolecular reactions, the initial concentrations of the reactants must be involved in the correction process. If we have different concentrations for both reactants (= AB case), the most obvious way would be to calculate that u value which obeys eqn. (7) for the second-order case, i.e. which yields $M = 0.013$ kJ/mole. However, in contrast to the first- or second-order case, a theoretical mathematical derivation of an equation such as eqn. (6) seems impossible. Thus, rate model curves using different initial concentrations of the reactants and varied activation data were generated and evaluated by the computer in order to estimate the approximate values of d , a , and b in eqn. (6).

The results of these computations applied to reactions 6, 9, and 17 (ref. 2) are not very different so that general validity of the constants d , a , and b can be assumed (Table 4). Consequently, $\ln \hat{k}(t)$ in eqn. (3) is obtained from $[A]_0$, $[B]_0$ and u_m using eqn. (19).

$$-\ln \hat{k}(t) = \ln u_m \div 0.19 \ln [A]_0 \div 0.75 \ln [B]_0 - 0.14 \quad (19)$$

TABLE 4

LOGARITHM OF THE RATIO OF HALF-WIDTH RATE CONSTANTS

$$\ln \frac{k_2}{k_1} = \frac{R}{E} (\ln k_m + \ln u_m + 0.75 \ln [A]_0 + 0.16 \ln [B]_0 - 0.14)$$

for three bimolecular reactions (Nos. 6, 9 and 17 in ref. 2)

$[A]_0$	$\frac{[B]_0}{[A]_0}$						
	1.0	1.5	2.0	3.0	5.0	∞	
1	3.237 ± 0.011 ^a	2.962 ± 0.045	2.750 ± 0.031	2.563 ± 0.033	2.436 ^b	2.25	
0.5	3.202 ± 0.030	2.867 ± 0.025	2.716 ± 0.029	2.416 ± 0.020	2.267	2.25	
0.1	3.244 ± 0.057	2.930 ± 0.021	2.746 ± 0.031	2.428 ± 0.031	2.329	2.25	
0.01	3.243 ± 0.033	2.955 ± 0.023	2.439 ± 0.014	2.439 ± 0.014	2.367	2.25	
Mean values	3.232 ± 0.020	2.929 ± 0.043	2.740 ± 0.016	2.459 ± 0.070	2.350 ± 0.071	2.25	
Expression below ^c	3.232	3.201	3.160	3.050	3.117	3.05	

^a Standard error.^b Reaction 9 only.^c The expression $\ln \frac{k_2}{k_1} = 0.5 \ln (1 - \ln q)$ is nearly independent of $q = [B]_0/[A]_0$ (cf. eqn. (26)):

$$3.135 \pm 0.031.$$

Therefore, an experimental DTA curve can be tested by estimation of the appropriate $u(t)$ for eqn. (7) by performing the following calculations.

(1) Activation energy and frequency factor from the temperature dependence of the rate constants obtained from eqn. (9).

(2) u_m by using eqn. (3) and $\tilde{k}(t) = 1/u_m$ in a rapidly converging iteration.

(3) $\ln \tilde{k}(t)$ from eqn. (19).

(4) u_2 (second-order) from eqn. (3) by insertion of $\ln \tilde{k}(t)$

The operations (2)-(4) had also been accomplished with the model curves using assumed activation data. In order to now use eqn. (7) as a criterion, the half-width has to be corrected with adequate superpositions of eqns. (1) and (17) or, for the shape index, of eqns. (2) and (18). We stated that linear superpositions will suffice; a suitable weight factor is

$$w = \ln \frac{c(q-1) + 1.6}{q + 0.6} \quad (20)$$

when

$$q = \frac{[B]_0}{[A]_0} \quad ([B]_0 \geq [A]_0) \quad (21)$$

(Pseudo-unimolecular process, $w = 1$; bimolecular process, $w = 0$).

Then, half-width and shape index of the corresponding rate curves are obtained by the equations

$$h_{xAB} = h_{x1} w + h_{x2} (1 - w) \quad (22)$$

$$S_{xAB} = S_{x1} w + S_{x2} (1 - w) \quad (23)$$

The corresponding reaction type index is calculated from u_2 and h_{xAB} .

$$M_{AB} = \frac{R m u_2}{(\log e)^2 h_{xAB}} \quad (24)$$

We have confirmed that S_{xAB} and M_{AB} may be recalculated to the ratio 1:1 of the reactants by the use of eqns. (7) and (20)

$$S_{x2} = S_{xAB} (1 + w) \quad (25)$$

$$M_2 = M_{AB} \frac{3.2 - w}{3.2} \quad (26)$$

since the shape index of a first-order rate curve (0.56 ± 0.02) is nearly half of the shape index of a second-order curve and since $M_1 = (1.5 \pm 0.1) M_2$ (Table 4; cf. ref. 6).

If we compare a reactant of unit concentration which formally undergoes a n -order reaction, there is the following general dependence of the reaction type index on the reaction order, n (ref. 7)

$$M = \frac{R (\ln 10)^2}{2.25 n^{0.52}} \approx \frac{4.185 \times 10^{-2}}{1 + 2S} \quad (27)$$

[cf. the expression (23) for the shape index in ref. 2]. Consequently, for complex reactions or even simple bimolecular reactions as discussed here two different "reaction orders" are to be expected (obtained from either S or M). In the case of an accurate "elementary" process of any order n , however, the coefficient

$$I = 23.9 M (1 + 2S) \quad (28)$$

obtained from eqn. (27) is nearly unity when M has the dimension kJ/mole K.

VI. EXAMPLES

Using heating rates of 0.5-3 K/min, the relationships presented were proven to be generally valid. Though the correction formulae (6), (17)-(20), (22), (23) and (25)-(28) are empirical, they can serve as a satisfactory means for characterizing bimolecular reactions kinetically. The fact that the results are approximate does not restrict the accuracy of the kinetic results at all since the activation parameters were obtained by the use of the accurate expressions, (8) or (9).

However, the accuracy of unique activation parameters may be nonsensical if the reaction is complex, i.e. if the reaction consists of several parallel or consecutive

TABLE 5

OVERALL KINETIC DATA OF DIELS-ALDER REACTIONS OF CYCLOPENTADIENE WITH *trans*-CYCLOOCTENONE-2 IN METHYLCYCLOHEXANE (= REACTION A, NOS. 1-6) AND WITH CYCLOOCTADIENE-(1,5) IN TOLUENE (= REACTION B, NOS. 7-10)

No.	[A] ₀ (mole/ dm ³)	[B] ₀ (mole/ dm ³)	E (kJ/ mole)	log k ₂ (min)	n ₂ (min)	S _{2,AB}	S ₂₂	M _{1AB} (= 10 ²)	M ₂ (= 10 ²)	I
1	0.10	0.10	45.6	8.8	7.6		0.53		16.7	0.82
2	0.10	0.50	41.9	7.9	8.6	0.56	1.20	19.5	14.4	0.99
3	0.50	0.50	58.1	11.6	8.5		0.86		16.7	1.09
4	0.50	0.54	47.7	9.3	7.3	0.93	1.01	13.4	12.7	0.87
5	0.40	1.00	42.3	7.9	7.7	1.10	1.80	16.1	13.1	1.29
6	0.22	1.04	49.4	9.7	8.2	0.50	0.91	17.7	12.9	0.82
Average values			47.5 ± 2.4*				1.21 ± 0.21		14.4 ± 0.7	0.98 ± 0.05
7	0.20	0.20	49.5	8.6	9.9		1.20		12.6	1.02
8	0.10	0.40	36.8	6.2	11.9	0.42	0.73	18.9	12.6	0.83
9	0.18	1.00	39.3	8.8	5.8	0.67	1.22	17.7	13.1	0.99
10	0.18	1.00	31.5	5.8	9.8	0.62	1.13	19.0	14.1	1.02
Average			39.4 ± 3.8		7.3 ± 0.8		1.07 ± 0.11		13.1 ± 0.4	0.97 ± 0.05
Second-order (theory)							1.15		13.0	1.00

m = 1.5 K/min; methylcyclohexane: $\epsilon = 0.15 + 0.79 \exp(-1038.7)$; toluene: $\epsilon = 0.17 + 36 \exp(-2130.7)$ [cf. eqn. (9)].

* Standard errors.

steps. Hence, the values of the mechanistic coordinates M and S represent a clue for the justification and signification of experimental kinetic data. From our experiments involving very different types of reactions in solution, it must be concluded that these coordinates are extremely sensitive to side reactions caused, for example, by contaminations.

Table 5 presents the results for two typical Diels-Alder reactions of cyclo-octane derivatives starting at 190-200 K^o. Though the correlation coefficients for a straight line approach of $\ln k$ vs. $1/T$ are between 0.980 and 0.998, the shape indices show considerable variations, even before the correction, which are not only based on the non-stoichiometric ratio of the reactants. The reaction type indices M_2 show minor variations, especially for the cyclooctadiene reaction. The mean values of S_{22} and M_2 nearly agree with the theoretical values for an elementary second-order reaction, whereas the I coefficients [eqn. (28)] show considerable deviations from unity in most of the AB cases.



For small concentrations of cyclooctenone and a stoichiometric amount of cyclopentadiene, there is only a very poor agreement of S , M , and I with the theoretical values signalling distortions in the progress of the reaction.

Table 6 summarizes results obtained from other reactions. Experiment Nos.

TABLE 6

ACTIVATION DATA, SPECIFIC TEMPERATURE DEPENDENCIES AND MECHANISTIC COORDINATES FOR SOME BIMOLECULAR REACTIONS IN SOLUTION

Heating rate ≈ 1.5 K/min.

Reaction	Reactants (solvent)	E	$\log k_a$	α_2	S_{eq}	S_{eq}	M_{eq}	l	Type ^a
11	C	0.076 H ₂ F ^b + 0.076 PO ₂ (THF)	43.9 { 40.2 83.7 }	10.2	7.7	0.75	12.9	1.13	P
		computer simulation:							
		0.062 2,5-dimethyl-1,3,4-F	9.0 (enthalpy: 502) } concurrent 16.3 (enthalpy: 377) } reactions						2
12	D	0.062 2,5-dimethyl-1,3,4-F + 0.092 PO ₂ (THF)	88.7	16.8	10.0	1.01	13.3	1.01	AB
13	E	computer simulation: 0.09 hydroxymethyl-1,3,4-F + 0.4 PO ₂ (THF)	93.7 48.6	16.7 10.3	9.7	1.42	16.5	0.96	AB/P
14	F	computer simulation: 0.09 2-chloromethyl-1,3,4-F + 0.09 PO ₂ (THF)	48.2 59.9	10.2 (cf. fig. 2) 13.3	8.0	1.00	13.4	0.90	AB 2/P
15	G	0.25 isobutylidene-indanone(1,3) ^b + 0.25 H ₂ C=C(OCCl ₂) ₂ (toluene)	{ 63.6 84.9 }	13.9 (enthalpy: 368) } concurrent 16.3 (enthalpy: 272) } reactions	9.4	1.10	12.8	0.96	1 2 2
16	H	computer simulation: 0.25 benzene-bisadduct + 0.5 butadiene (perylene)	56.9 64.0	11.3 16.5	5.3	0.78	20.3	1.20	P or P'
17	I	computer simulation: 0.25 (C ₆ O) ₂ PO ₂ ^c	63.8	16.5					
18		0.4  (C ₁₁ H ₂ Cl ₂) 0.10 (C ₆ O) ₂ PO ₂ ^c + 1.3  (C ₁₁ H ₂ Cl ₂)	50.6 59.8 59.8	10.1 11.2 11.1 (cf. Fig. 3)	10.3 9.5	1.20 1.04	14.7 18.5	0.97 0.91	AB AB
Theory:		computer simulation: second-order reaction first-order reaction							
					0.56	1.15	19.7	1.00	2
							13.0	1.00	1

^a 1, Pseudo-unimolecular reaction; 2, second-order reaction; AB, bimolecular reaction; P, concurrent decomposition; P', consecutive step(s).^b See text.

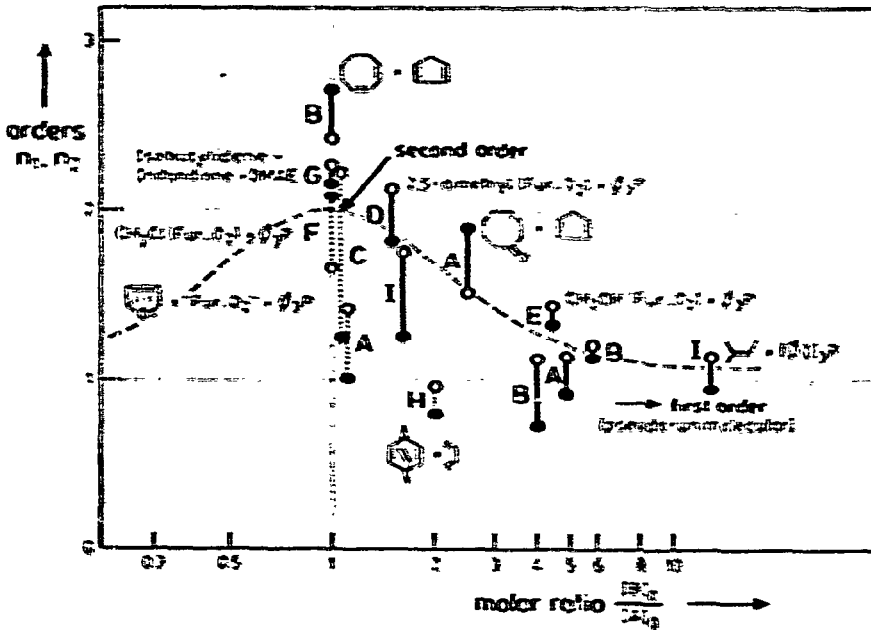


Fig. 1. Two kinds of non-isothermal "reaction order" in some bimolecular reactions (cf. Tables 5 and 6). ●, n_1 (calculated from S); ○, n_2 (calculated from M); ●...○, complex reaction.

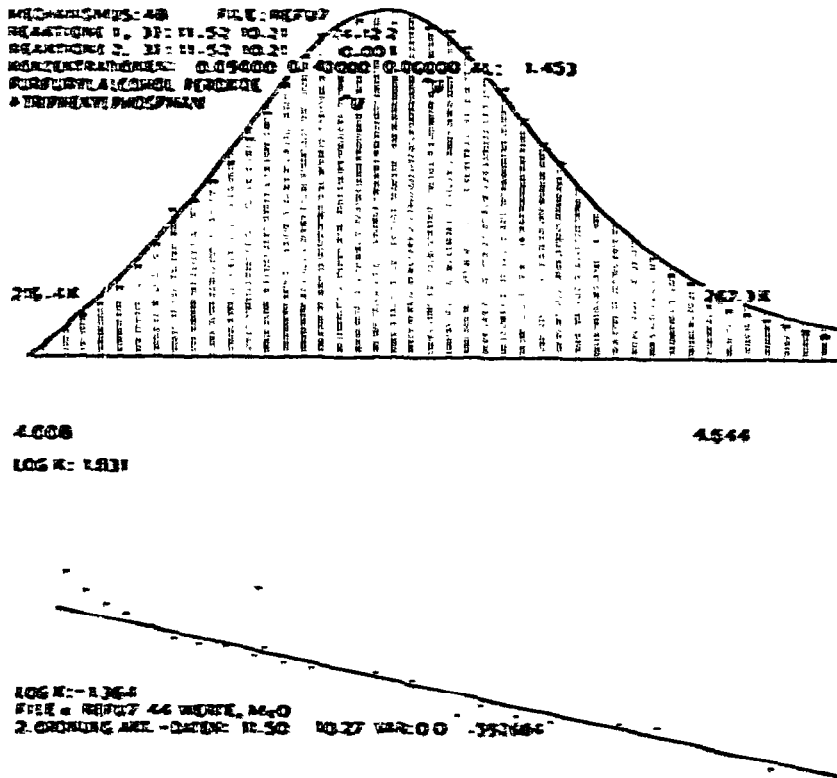


Fig. 2. Original computer sheet, experiment No. 13. Above, comparison of curves. Vertical lines, experimental curves; continuous line, theoretical curve; data. E (kcal/mole), $\log k_{\infty}$ (k_{∞} /min), ΔH (kcal/mole). Below, Arrhenius plots. The best (weighted) overall straight line is demonstrated. Limiting values of $\log k$ and of $1000/T$ are typed out.

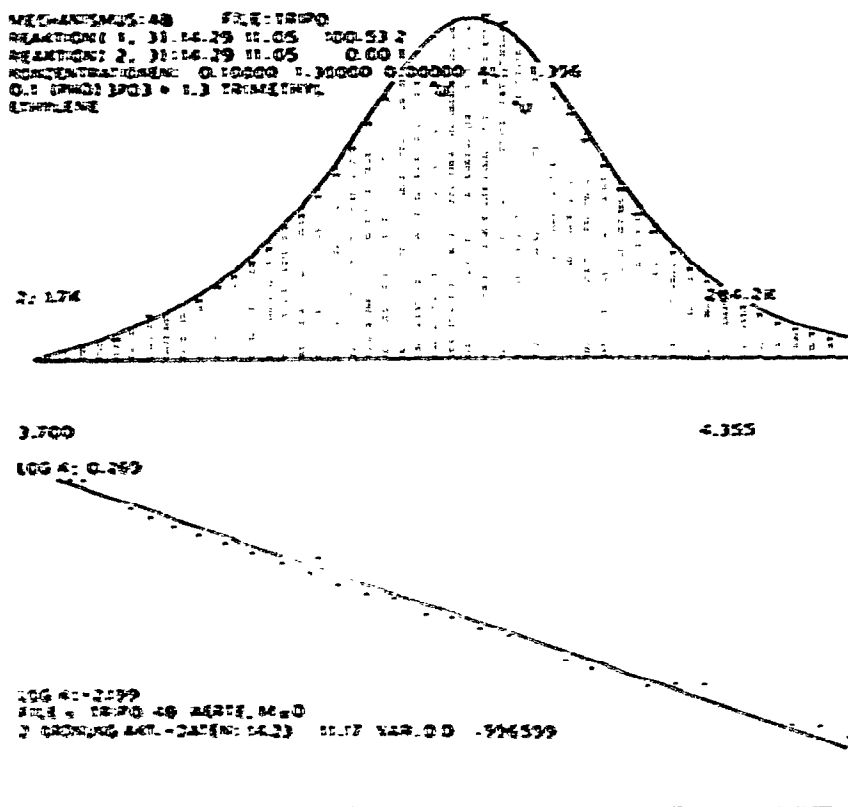


Fig. 3. Original computer sheet, experiment No. 18. Above, comparison of curves. Vertical lines, experimental curves; continuous line, theoretical curve; data, E (kcal/mole), $\log k_x$ (k_x /min), ΔH (kcal/mole). Below, Arrhenius plots. The best (weighted) overall straight line is demonstrated. Limiting values of $\log k$ and of $1000/T$ are typed out.

11-14 cover DTA curves of the reduction reactions of different ozonid-like epidioxydihydrofuranes with triphenylphosphane⁹ ($\Delta H \approx -330$ kJ/mole), Nos. 15, 16 are special Diels-Alder reactions, No. 16 is induced with UV light¹¹ ($\Delta H \approx -60$ kJ/mole), and Nos. 17 and 18 are due to a thermal oxidation process which leads to hydroperoxides¹² ($\Delta H \approx -400$ kJ/mole). These bimolecular reactions show initial temperatures between 176 and 265 K and M values which agree well with the theoretical values (12.8 ± 0.24 instead of 13.0×10^{-3} kJ/mole K). The extrapolated shape indices $S_{x,2}$ again show stronger variations ($S_{x,2} = 0.92 \pm 0.19$ instead of 1.15) which presumably signals a certain complexity of the processes as is also indicated by the considerable deviations of I from unity.

These results are confirmed by the comparison of the formal reaction orders n_1 and n_2 , determined from $S_{x,2}$ (or $S_{x,AB}$) and from M , respectively. As Fig. 1 demonstrates, these values are often different from each other: only in such cases where an approximate second-order reaction (Nos. 3, 7, 14, 15) or pseudo-unimolecular reaction (Nos. 2, 6, 9, 10, 18) may be assumed are the orders in rough agreement with each other (complex conditions excepted).

For additional confirmation of the activation data obtained, theoretical DTA

curves were generated by using the synthetic computer program in order to reproduce the experimental curves. On the VT 55 graphic terminal, both curves were projected and visually compared. Figures 2 and 3 give two examples of Table 6; the same activation energies as those obtained by the analytical program were used, and frequency factor and enthalpy were varied until the best coincidence was reached. In experiment Nos. 11 and 14, two assumed concurrent reactions of different order revealed a better fit than only one reaction.

VII. DISCUSSION AND OUTLOOK

The half-width and shape index of the DTA curve of a second-order reaction are similarly related to the kinetic data, to the kinetic cell constant and to the maximum temperature difference as for a first-order reaction. The influence of the kinetic parameters may be preferentially described by one quantity, the specific time μ . From the involvement of the product μc in the fractional algebraic expressions (17) and (18) for h_{ideal} and S_{ideal} , it can be concluded that for decreasing μ or c , the kinetic information obtained is restricted in favour of information on the heat decay behaviour. In general, the kinetic information is also decreased with the progress of the reaction; however, the conditions for the kinetic evaluation in the last part of the DTA curve are not as unfavourable as for a first-order reaction; therefore, more than 85% of the total curve can usually be evaluated for μ values between 4 and 8 (ref. 7).

On the other hand, it must be tedious to search for examples of bimolecular second-order reactions which accurately obey the "elementary reaction" criteria of non-isothermal reaction kinetics, since these permit an even smaller range of reactions than does the order concept in isothermal kinetics. Another reason is surely the law of mass action which states that the 1:1 ratio is most unfavourable for the rapid advancement of a bimolecular reaction. Thus, side reactions may gain strength, whereas reversible steps may only become effective for endothermic or weakly exothermic reactions.

Turning to bimolecular reactions with non-stoichiometric reactants, the experiments reveal a certain similarity to the formal n -order reaction involving only one reactant and following the rate law

$$-\frac{d[A]}{dt} = k_{\pm} e^{-E_i/RT} [A]^n \quad (29)$$

with fractional n values between 1 and 2. However, the two particular reaction orders n_1 (via S) and n_2 (via M) in general differ from each other because the rate laws differ, while for a true n -order reaction they must be identical.

Hence, the I coefficient cannot be exactly unity for all of such bimolecular reaction plots even if there are no distortions. Therefore, the extrapolated values $S_{\pm 2}$ and $M_{\pm 2}$ are more suitable quantities for indicating the presence of distortions than the I value. The latter is more adapted to an "order-of-reaction" diagnosis if a very great excess of one of the reactants or only one reactant was used; in these

cases, $l = 1$ means that the reaction can be described by the n -order law, eqn. (29), which is usual also in the field of solid state kinetics though only part of the rate laws occurring there are covered by this equation¹³⁻¹⁴.

Under such heterogenic conditions, the n values are usually less than unity whereas the majority of our bimolecular experiments in solution lead to orders n_1 and n_2 between 0.92 and 2.4 (No. 8 expected). Although there is a general tendency to decreasing n with increasing $[B]_0 : [A]_0$ ratio, it is obvious that in many experiments striking deviations of n_1 and n_2 from each other can only be explained by the complex character of the reactions studied.

This view is strengthened by earlier preparative results. Indeed, the unstable epidioxydihydrofuran in reaction C tends to isomerize to pseudo-maleic aldehyde acid so that only 70% maleic dialdehyde was found after the reduction¹⁵. Similarly, the reduction of the 2-hydroxy derivative of this epidioxide (reaction E) may be accompanied by a rupture of the side chain yielding formic acid¹². Finally, the very reactive photoadduct from benzene and butadiene adds butadiene yielding ~86% of the Diels-Alder-type adduct apart from a 2:2 adduct obtained by homodimerization and other kinds of 2:2 adducts (reaction H)¹¹.

In conclusion, the mechanistic coordinates S and M , when corrected for rate curves and, in the case of bimolecular reactions, to an 1:1 ratio of the reactants, represent fundamental quantities in non-isothermal reaction kinetics at linearly increasing temperatures, since they allow classification of all reactions in principle. For reactions in solution, all experiments can be assigned to five basic groups, namely (1) first-order reactions (unimolecular or pseudo-unimolecular); (2) second-order reactions (bimolecular, $[A]_0 = [B]_0$); (3) bimolecular reactions with non-stoichiometric initial ratio of the reactants; (4) complex reactions following the rate law of n order [eqn. (29); $n \neq 1$, $n \neq 2$]; (5) other complex reactions.

Our preliminary experience with 62 different reactions, partially with varied solvents, is that the majority of the DTA curves obtained belong to the last group. We have described ways to classify such complex reactions starting from the activation data of the initiating reaction¹⁶ whilst in this publication the overall data was used: the accuracy of overall data is better and the absolute frequency factor of the initiating reaction can only be calculated when the enthalpy of the initiating reaction is exactly known. However, the apparent frequency factor determined from the simplified Borchardt-Daniels equation at the start of the curve or even the overall data could also be used when the model diagrams for the basic complex types of reaction¹⁶ were recalculated by the computer.

Thus, we intend to increase our knowledge on handling of complex reactions and to test the utility of the new concepts by using a representative material on reactions in solution also stemming from other investigators.

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