ON THE ORDER OF INFLUENCED REACTIONS

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The reaction order of catalyzed and inhibited reactions with respect to c_I, the concentration of the influencing substance had been analyzed according to the order definition $\nu = \partial \log w / \partial \log c_I$. For certain cases of the chain influencing this expression had been represented with characteristics of the reaction and its possible variation types had been established. The explanation dealt also with the connection between the reaction order and the influencing factor of the reaction. The considerations had been compared with the experiments, too.

The order of catalyzed and inhibited (summarized: influenced) reactions with respect to the concentration of the influencing substance (catalyst or inhibitor) is not such an exactly defined concept as that of the order of the reactants. As a matter of fact, the concentration dependence

$$w = f(c_a,\ c_b,\ \ldots\ ;\ c_I) \tag{1}$$

of the reaction rate on the concentrations c_a, c_b, ... of the reactants A, B, ... and c_I of the influencing substance I can be written only in fortunate cases in the form

$$w = k c_a^{n_a} c_b^{n_b} \ldots \phi(c_I) \tag{2}$$

expressing the separability of the effect of the influencing substance, where n_a, n_b, ... denote the reaction orders with respect to concentrations c_a, c_b, ..., and k is a constant. From these representations of the reaction rate clearly appears that in general case the process cannot be characterized by a reaction order with respect to concentration c_I even in the relatively simple case of representation (2) because the functions f and ϕ do not change according to any power. (In case of general representation (1) even the reaction order with respect to the concentration of the reactants loses its meaning.)

This hardness in characterizing the reaction by a reaction order is expressed most doubtless in the logarithmic plotting of log w versus log c_I. As it is well-known, this plotting shows linearity only when the reaction has a well-defined order in which case the order agrees with the slop of the plotting. This definiteness of the order is obviously equivalent with the constancy of the derivative $\nu = \dfrac{\partial \log w}{\partial \log c_I}$. On the contrary, if the previous derivative changes, then it means that no order in the usual sense is defined.

On the other hand there are arguments supporting the introduction of this derivative

$$v = \frac{\partial \log w}{\partial \log c_I} \tag{3}$$

as a generalized reaction order even when in the original meaning the concept seems to be sensless. Such an argument was presented by the endeavours to compare the explanation for the influencing of thermal decomposition of propionic aldehyde by nitrogen monoxide reported by SZABÓ and MÁRTA [1] with HINSHELWOOD and collaborators' interpretation in similar field of influenced thermal decompositions [2—5]. The latter authors characterize the effect of the influencing substance by a reaction order, while SZABÓ and MÁRTA do this by introducing the concept of the influencing factor.

The comparison of the two interpretations becomes possible when the changing of the derivative (3) is not regarded as a criterion of lack of order and v defined by (3) is considered as a reaction order varying during the reaction course. With the aim of realizing this comparison let the scheme of influenced chain reactions developed by SZABÓ, HUHN and BERGH be regarded [6, 7].

According to this scheme the influencing substance I exerts its effect on the chain

$$\mathrm{A} + \mathrm{X} \rightarrow \qquad (k_2^I)$$

developed by radicals X formed in the initiating reaction

$$\mathrm{A} \rightarrow \mathrm{X} + \ldots \qquad (k_1)$$

in the way of forming stabilized radicals

$$\mathrm{IX} \rightleftharpoons \mathrm{I} + \mathrm{X} \qquad \text{(with equlibrium constant } K).$$

also being able to continue the chains or terminate them. Bearing in mind this possibility in the mechanism of the reaction it has been shown that the stationary concentration of the radicals can be given in the form

$$[X]_{st} = x_{st} = f(c_a,\ c_I) \tag{4}$$

of a simple algebraic function containing only square roots as irrational elements. Considering this structure of x_{st} and the presence of the chain

$$\mathrm{A} + \mathrm{IX} \rightarrow \qquad (k_2^{II})$$

the reaction rate can be expressed by

$$\begin{aligned} w &= k_2^I c_a f(c_a, c_I) + k_2^{II} \frac{c_a}{K} f(c_a, c_I) = \\ &= k_2^I c_a (1 + \beta c_I) f(c_a, c_I), \end{aligned} \tag{5}$$

where β denotes the ratio $k_2^{II}/k_2^I K$. The expression is therefore of the general type (1) with regard of the feature of function $f(c_a, c_I)$ mentioned before.

In the fortunate case when all the terminating reactions

$$\mathrm{X} + \mathrm{X} \rightarrow \qquad (k_4^I)$$
$$\mathrm{X} + \mathrm{IX} \rightarrow \qquad (k_4^{II})$$
$$\mathrm{IX} + \mathrm{IX} \rightarrow \qquad (k_4^{III})$$

are bimolecular, the effect of the influencing substance can be separated. For this case in the referred papers the following rate expressions have been given:

$$w_{\text{infl.}} = k_2^{I} \sqrt{\frac{k_1}{k_4^I}}\, c_a^{3/2} \frac{1+\beta c_I}{\sqrt{1+2\delta_1 c_I + \delta_2 c_I^2}} \tag{6}$$

and

$$w_{\text{non infl.}} = k_2^{I} \sqrt{\frac{k_1}{k_4^I}}\, c_a^{3/2}, \tag{6$_0$}$$

where $\delta_1 = k_4^{II}/k_4^I K$ and $\delta_2 = k_4^{III}/k_4^I K^2$. (The latter equation is included in the previous one with $c_I = 0$.) As it can be seen easily, the effect of the influencing species is expressed with the factor

$$F(c_I) = \frac{1+\beta c_I}{\sqrt{1+2\delta_1 c_I + \delta_2 c_I^2}} \tag{7}$$

defined previously as the influencing factor of the reaction.

This rate expression is obviously of the form (2), accordingly the order defined by it can be represented in a simpler way as given by (3), namely by

$$v = \frac{d \log F(c_I)}{d \log c_I} = \frac{c_I}{F(c_I)} \frac{dF(c_I)}{dc_I}, \tag{8}$$

or in its developing

$$v = c_I \left\{ \frac{\beta}{1+\beta c_I} - \frac{\delta_1 + \delta_2 c_I}{1+2\delta_1 c_I + \delta_2 c_I^2} \right\} = \frac{1+\delta_1 c_I}{1+2\delta_1 c_I + \delta_2 c_I^2} - \frac{1}{1+\beta c_I}. \tag{9}$$

A short judgement of this expression shows at once that its magnitude may correspond to a reaction order with respect to c_I lying between —1 and +1, depending on the ratio of the terms 1, βc_I, $\delta_1 c_I$ and $\delta_2 c_I^2$. (This is sufficiently apparent already from the form (7) of the influencing factor occuring in the expression of $w_{\text{infl.}}$ given by (6).) *E. g.* when in the actual concentration range $\beta c_I \gg 1$ and $2\delta_1 c_I \gg 1 + \delta_2 c_I^2$ then the order becomes nearly 1/2; or in an other case when $1 \gg \beta c_I$ and $\delta_2 c_I^2 \gg 1 + 2\delta_1 c_I$ then the order will be nearly —1. At the same time, it is obvious that the ratio of the magnitudes in question, with varying c_I also varies, a fact which implies the possibility of the change of order with varying c_I.

For a more precise evaluation of this change let the order expressions (8) and (9) be regarded. It is almost obvious that $v = 0$ for the two limiting cases $c_I = 0$ and $c_I = \infty$. As v is evidently not a constant, it must have at least an extreme value in the range $0 < c_I < \infty$. When the differential quotient dv/dc_I is evaluated then it follows in a few steps

$$\frac{dv}{dc_I}=\frac{\beta(1+2\delta_1c_I+\delta_2c_I^2)^2-(1+\beta c_I)^2(\delta_1+2\delta_2c_I+\delta_1\delta_2c_I^2)}{(1+\beta c_I^2)\,(1+2\delta_1c_I+\delta_2c_I^2)^2}\equiv$$

$$\equiv\frac{(\beta-\delta_1)+2(\beta\delta_1-\delta_2)c_I+\{3\beta\delta_1(\delta_1-\beta)+(2\beta+\delta_1)(\beta\delta_1-\delta_2)\}\,c_I^2}{(1+\beta c_I^2)\,(1+2\delta_1c_I+\delta_2c_I^2)^2}+$$

$$+\frac{2\beta\delta_2(\delta_1-\beta)c_I^3+\beta\delta_2(\delta_2-\beta\delta_1)c_I^4}{(1+\beta c_I^2)\,(1+2\delta_1c_I+\delta_2c_I^2)^2}. \qquad (10)$$

Considering the fact that dv/dc_I has at least one 0-place in the positive concentration range, from this form of the derivative it can be seen easily that equation $dv/dc_I = 0$ has one or two positive roots according to the signs of expressions $(\beta-\delta_1)$ and $(\beta\delta_1-\delta_2)$ agree or disagree. (In the first case the set of the coefficients contains only one change in the signs, in the second, however, two. Since the number of roots is at least one, the statement follows immediately according to DESCARTES' rule.) Therefore the feature of the variation of v can be given by the following types:

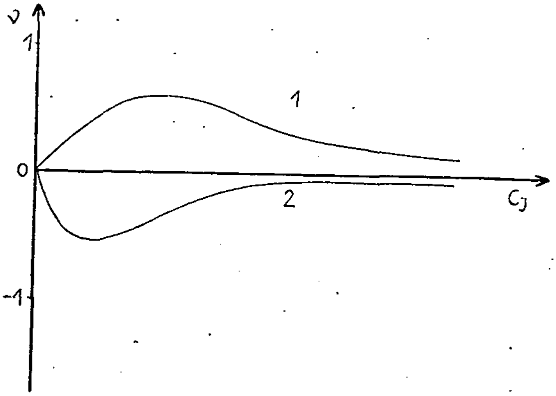

Fig. 1. The change of the order for monotonous influencing. 1 catalysis, 2 inhibition

a) $dv/dc_I = 0$ having only one positive root the order has a single extreme as represented by two type of curves on Fig. 1.

b) $dv/dc_I = 0$ having two positive roots the order has two extremes as illustrated by curves 1 and 2 on Fig. 2.

Regarding the latter curves it has to be mentioned that their 0-place has an evident chemical meaning, it denotes namely that concentration of the influencing substance at which the influencing is extreme. This is apparent from form (8) of v. As explained in the previous papers, this concentration can be given by

$$c_{\text{extr.}}=\frac{\beta-\delta_1}{\delta_2-\beta\delta_1} \qquad (11)$$

whereby also the meaning of the change or consecution in the signs of $(\beta-\delta_1)$

and $(\beta\delta_1-\delta_2)$ becomes clear. For influencing with extreme the signs in question disagree, while for influencing without extreme they agree. Hence the variation of v behaves according to types of Fig. 1 or Fig. 2 depending on whether the influencing phenomenon is monotonous or it has an extreme with varying c_I. Between the characteristic difference of types 1 and 2 (in both Fig. 1 and 2) and the chemical feature of the influencing phenomenon there is also a typical correspondence. The initial slope of the curve $v = v(c)$ at $c_I = 0$ evidently seems to be equal to $(\beta—\delta_1)$ which is at the same time the initial slope of the curve $F = F(c_I)$. This means that the reaction order is in the initial stage at $c_I = 0$ in the same meaning increasing or decreasing as the influencing factor. Therefore the change of the reaction order can be characterized by curves of types 1 or 2 depending on whether the influencing begins with catalysis or inhibition, respectively.

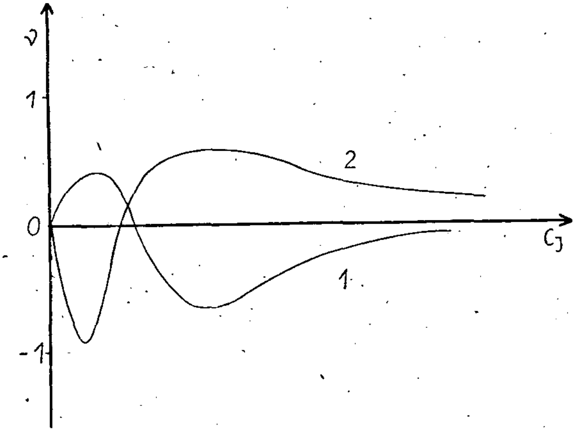

Fig. 2. The change of the order for influencing with extreme. 1 influencing beginning with catalysis, 2 influencing beginning with inhibition

From the variability of v outlined before, it can be seen that a rough evaluation of the reaction order may lead to a false interpretation of the process. For example, when this order seems in a concentration range to be about 1/2, then it is a hasty conclusion to regard the reaction as a half order one with respect to the concentration of the influencing substance. And it would be quite wrong to draw extreme conclusions from an unusual concrete value of this order, as *e. g.* to look for a peculiar mechanism in case of an order nearly equal to 1/3.

To illustrate this establishment as well as to demonstrate the variation of the order defined by (3) let the results of the investigations relating the thermal decomposition of propionic aldehyde, elaborated by SZABÓ and MÁRTA, be considered. According to these authors' statements this decomposition proceeds according to chain reaction developed by C_2H_5 radicals produced in the initiating reaction $C_2H_5CHO \rightarrow C_2H_5+CHO$ (which is followed by the very fast reaction $CHO+ +C_2H_5CHO \rightarrow C_2H_5CO+CO+H_2$) and disappearing in the terminating reaction $C_2H_5+C_2H_5 \rightarrow C_2H_6+C_2H_4$. If nitrogen monoxide is added to the reaction then stabilized radicals, C_2H_5NO, will be formed also participating in the chain and terminating reactions as mentioned before and discussed in the papers referred [1], [6] and [7]. Considering these elementary steps, it is easy to show that the rate expressions of the reaction can be given by equations (6) and (6_0) — with the insignificant modification of replacing the constants k_1 and k_2^I by $2k_1$ and $2k_2^I$, respectively. (As a matter of fact, the initiating reaction produces two ethyl radicals and the chain consumes two aldehyde molecules in every step.) As a consequence of these rate formulae the influencing factor and followingly the order can be represented in form of equations (7) and (8)—(9), respectively.

Table I

The variation of the reaction order in the experiments at $t = 515$ °C with the initial aldehyde pressures $p_{\text{Ald.};\,0} = 150$ mm Hg

$\log c_I$	$\log F(c_I)$	$\nu = \dfrac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,255−1	0,892−1	
0,342−1	0,88 −1	−0,14
0,716−1	0,85 −1	−0,08
0,903−1	0,857−1	+0,037
0,301	0,954−1	+0,23
0,477	0,995−1	+0,24
0,716	0,083	+0,37
1,00	0,19	+0,38
1,23	0,294	+0,45
1,422	0,38	+0,447
1,686	0,506	+0,477
1,792	0,559	+0,50

Table II

The variation of the reaction order in the experiments at $t = 535$° C with the initial aldehyde pressures $p_{\text{Ald.};\,0} = 150$ mm Hg

$\log c_I$	$\log F(c_I)$	$\nu = \dfrac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,00 −1	0,924−1	
0,30 −1	0,869−1	−0,18
0,653−1	0,819−1	−0,14
0,813−1	0,819−1	0,00
0,255	0,869−1	+0,11
0,49	0,903−1	+0,144
0,857	0,045	+0,38
1,238	0,182	+0,35
1,556	0,338	+0,49
1,653	0,375	+0,38
1,806	0,435	+0,39

In the following tables (Table I and II) these values are grouped having evaluated them from the experimental data of SZABÓ and MÁRTA [1] by means of (3) and (8) and by replaceing the derivatives $d \log F(c_I)/d \log c_I$ by the quotients

$\Delta \log F(c_I)/\Delta \log c_I$. The data are plotted on Figs. 3—6 wich contain also the variation of reaction order calculated with the characteristic quantities β, δ_1 and δ_2 of the reaction according to (9), as well as the variation of the influencig factor. (All the curves are given in plotting versus $\log c_I$.)

As it seems immediately the plotting $\log F(c_I)$ *versus* $\log c_I$ shows in the range $0{,}6 < \log c < 2{,}0$ a quite satisfactory linearity with the slope of about 1/2. (This is demonstrated also by the curves $v = v(c_I)$ the maximum of wich lies very near to 1/2 in a wide concentration range where the variation is extremely slow.) In this way the reaction seems to be of a half order one in the concentration range in question without drawing any further conclusions regarding the mechanism of the reaction.

Table III

The variation of the reaction order in the experiments at $t = 550$ °C with the initial aldehyde pressures $p_{\text{Ald.}; 0} = 150$ mm Hg

$\log c_I$	$\log F(c_I)$	$v = \dfrac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,301−1	0,888−1	
0,58 −1	0,83 −1	−0,19
0,81 −1	0,79 −1	−0,17
0,95 −1	0,778−1	−0,10
0,114	0,81 −1	+0,19
0,204	0,83 −1	+0,28
0,58	0,903−1	+0,18
1,215	0,093	+0,29
1,33	0,146	+0,45
1,44	0,19	+0,41
1,78	0,33	+0,40

Table IV

The variation of the reaction order in the experiments at $t = 565$ °C with the initial aldehyde pressures $p_{\text{Ald.}; 0} = 150$ mm Hg

$\log c_I$	$\log F(c_I)$	$v = \dfrac{\Delta \log F(c_I)}{\Delta \log c_I}$
0,40−1	0,87 −1	
0,78−1	0,79 −1	−0,16
0,20	0,76 −1	−0,08
0,57	0,82 −1	+0,17
0,70	0,82 −1	+0,24
1,16	0,99 −1	+0,31
1,56	0,155−1	+0,43
1,66	0,22	+0,60
1,78	0,28	+0,51

It seems very probable that the results in HINSHELWOOD and coworkers' investigations, according to which the effect of the influencing substance would be summarized in a half order reaction with respect to the influencing species, have similar

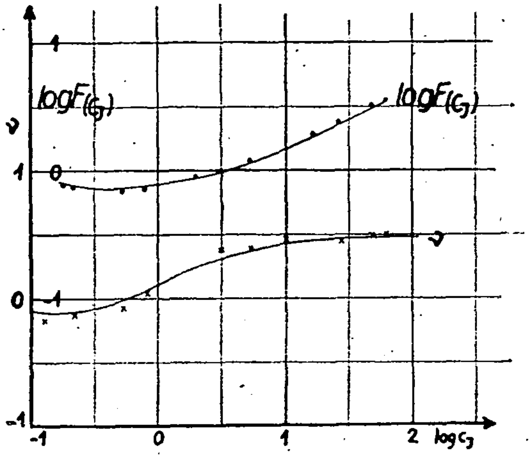

Fig. 3. The variation of the reaction order and the influencing factor in the experiments at $t = 515$ °C with the initial aldehyde pressure $p_{\text{Ald.; 0}} = 150$ mmHg. Continuous curve: calculated according to equation (7) and (9) with $\beta = 1{,}3$, $\delta^1 = 4{,}1$, $\delta_2 = 0{,}003$. ● and × : calculated directly from the experimental data

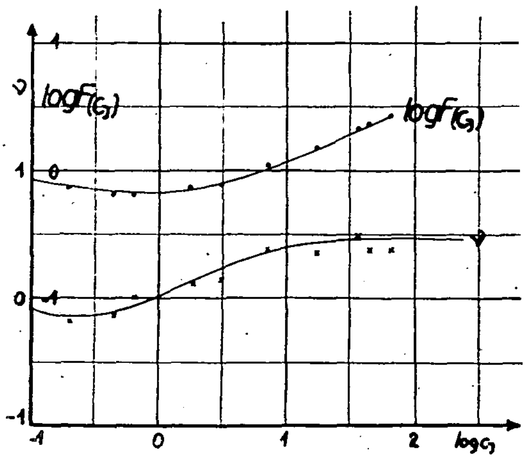

Fig. 4. The variation of the reaction order and the influencing factor in the experiments at $t = 535$°C with the initial aldehyde pressure $p_{\text{Ald.; 0}} = 150$ mmHg. Continuous curve: calculated according to equation (7) and (9) with $\beta = 0{,}85$, $\delta_1 = 3{,}1$, $\delta_2 = 0{,}0017$. ● and × : calculated directly from the experimental data

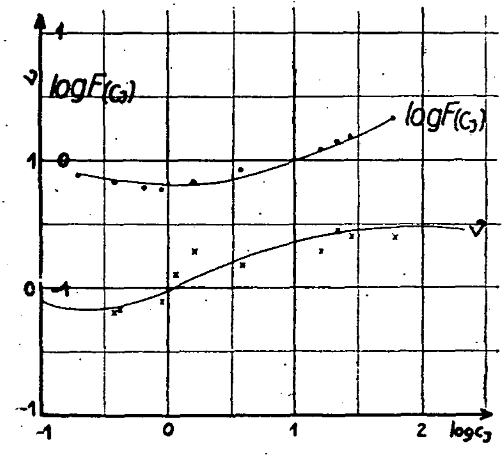

Fig. 5. The variation of the reaction order and the influencing factor in the experiments at $t = 550$°C with the initial aldehyde pressure $p_{\text{Ald.; 0}} = 150$ mmHg. Continuous curve: calculated according to equation (7) and (9) with $\beta = 0{,}65$, $\delta_1 = 2{,}75$, $\delta_2 = 0{,}0011$. ● and × : calculated directly from the experimental data

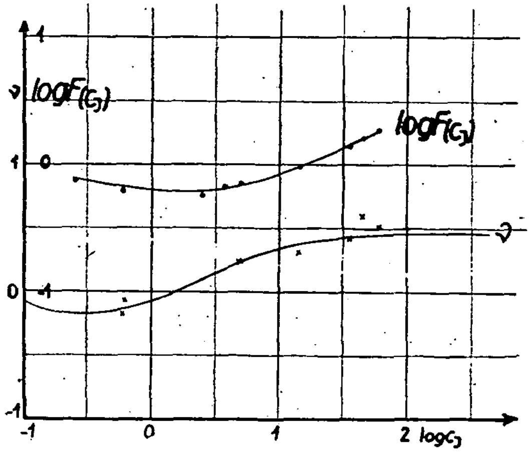

Fig. 6. The variation of the reaction order and the influencing factor in the experiments at $t = 565$°C with the initial aldehyde pressure $p_{\text{Ald.; 0}} = 150$ mmHg. Continuous curve: calculated according to equation (7) and (9) with $\beta = 0{,}50$, $\delta_1 = 2{,}30$, $\delta_2 = 0{,}0007$. ● and × : calculated directly from the experimental data

reason. These authors made their experiments with sufficiently high nitrogen monoxide concentrations under which circumstances the determination of the initial stage of the influencing curve did not occur.

From the explanation the conclusion must be drawn that in the possession of a reaction order of the influencing substance some care must be taken not to overestimate its significance. Apart from the fact that it cannot be regarded as an unequivocal characteristic of the reaction (because it is a locally defined concept) its origin also indicates that it must be regarded with an other view as the reaction order of the reactants. In fact the previously described variation of the influencing factor arises from those interactions by which the influencing species regulates the stationary concentration of the radicals. Thus the order defined for this concentration dependence of the reaction rate can be regarded more precisely not as an order of the reaction, but rather as the order of the influencing phenomenon. This is the proper view of the reaction order with respect to the concentration of the influencing substance which coincides with the essence of the mechanism of the influencing phenomenon and therefore promotes their investigation.

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ПОРЯДОК РЕАКЦИЙ ПОДВЕРЖЕННЫХ ВОЗДЕЙСТВИЮ

Ф. Марта и П. Хун

Авторы изучали порядок катализованных и ингибированных реакций в функции концентрации c_I влияющего материала на основе $\nu = \partial \log w/\partial \log c_I$.

Для нескольких случаев цепного воздействия авторы дали это выражение имея в виду характеристику реакций, и также установили возможные типы вариантов. Эта интерпретация далее раскрыла связь между порядком и фактором воздействия реакции.

Результаты этих соображений были сравнены с экспериментами.