287. Chemical Selectivities Disguised by Mass Diffusion. III. A Comparison of Two Versions of a Simple Model of Mixing-Disguised Reactions in Solution[1])

3rd Communication on the Selectivity of Chemical Processes[1])

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Summary

A simple mixing-reaction model has been developed [1] which allows a description and simulation of the coupling of the mass diffusion with the chemical reaction during the mixing process of two miscible reactant solutions. For competitive, consecutive as well as for competitive, parallel second-order reactions the general behaviour and the dependence of the product distribution on diffusion effects are calculated for semi-continuous reaction conditions using various simplifying assumptions. The usefulness of these assumptions is discussed with reference to the calculated predictions of two versions of the mixing-reaction model.

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1. Introduction. - For the purpose of rationalizing the path taken by reagents during their reaction to give the product it is convenient to subdivide a chemical reaction into various individual processes: At first the solutions of the reacting species have to be mixed together. This mixing process is accompanied by a molecular diffusion process in which the encounter complex is formed. Finally, this encounter complex can either dissociate, or the bond-making and bond-breaking events lead to the product. In the case of fast reactions the mixing process or the encounter complex formation can be the rate limiting step and hence affect the observed product distribution.

In Part I of this series [1] a simple mixing-reaction model was developed which allows a description of the coupling of the mass diffusion with the bond-making and bond-breaking events of a chemical reaction during the mixing process. The dependence of the product distribution on mass diffusion effects was simulated. In Part II of this series [2] the disguise of the chemical selectivity by the mixing process was demonstrated experimentally using the fast nitration with nitronium salts in aprotic solvents.

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[1]) Part II (2nd Communication) *cf.* [2].

In the present paper, the calculated predictions of two versions of the mixing-reaction model are compared. In contrast to version I [1], the new version II is expected to allow more accurate predictions to be made of the product distribution in mixing-disguised batch-wise reaction systems such as those encountered in everyday laboratory syntheses.

2. The Mixing-Reaction Model. - The concept of the presented model has already been described in detail [1]. It is based on the assumption that during the addition of one reactant solution to another, liquid elements, so-called eddies, are formed. The mean size of these eddies, *i.e.* the segregation length, will be a function of the solvent and of the intensity of the turbulence [3] [4]. The latter will depend on the kinetic energy added to the system, for example, by mechanical stirring. It will also depend on the viscosity of the solvent.

The turbulent flow of a liquid consists of disorderly displacements of fluid elements. According to *Kolmogoroff* [4] these displacements can be thought of as a superposition of pulsations of successively increasing frequency. Such a process of successive refinement of turbulent pulsations may be continued until, for pulsations of some sufficiently large order n, the kinetic energy of the liquid elements is viscously dissipated as heat thus preventing the formation of pulsations of order n + 1. The characteristic length of the liquid elements (eddies) which are associated with the pulsations of the order n, is defined as the *Kolmogoroff* turbulence microscale.

In our mixing-reaction model it is assumed as a first approximation that the dispersion of the eddies throughout the whole liquid is much faster than the molecular diffusion within them, and that the eddies are spherical with a mean radius $\bar{R}$ of the order of the *Kolmogoroff* turbulence microscale.

For the mathematical description of the mixing-reaction-process the equation of continuity is used:

$$\frac{\partial [i]}{\partial t} = -1000(\nabla \cdot \vec{N}_i) + r_i . \tag{1}$$

$[i]$ molar concentration of species i [M];
$\vec{N}_i$ molar flux of species i with respect to stationary coordinates [mol cm^{-2}s^{-1}];
t time [s];
r_i molar rate of production of species i by chemical reaction [M s^{-1}];
∇ 'del' or 'nabla' operator [cm^{-1}].

Equation (1) describes the change of molar concentration of the component i with respect to time at a fixed point in space. This change results from the motion of species i and its chemical reaction. Choosing the eddy as diffusion-reaction system and assuming constant diffusion coefficients, constant total molar concentration, zero molar average velocity[2]) and spherical eddies with constant mean radius, equation (1) becomes[3]):

$$\frac{\partial [i]}{\partial t} = D_i\left(\frac{\partial^2 [i]}{\partial r^2} + \frac{2}{r}\,\frac{\partial [i]}{\partial r}\right) + r_i . \tag{2}$$

D_i diffusion coefficient of species i [cm^{2}s^{-1}];
r polar coordinate [cm].

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[2]) The molar average velocity is understood to be the velocity caused by the bulk motion of the fluid within the eddy. If it is assumed that the bulk motion of the main component of the eddy fluid, namely the solvent, is zero, the molar average velocity can also be assumed to be zero.

[3]) For a more detailed derivation of equation (2) see [1].

The molar rate of production by chemical reaction, $\mathbf{r}_i$ in equation (2), can be replaced in a competitive, consecutive second-order reaction system *(Scheme 1)* by the expressions (3)-(6) and in a competitive, parallel second-order reaction system *(Scheme 2)* by the expressions (7)-(11).

Scheme 1

$$A+B \xrightarrow{k_1} R \quad \text{primary reaction}$$

$$R+B \xrightarrow{k_2} S \quad \text{secondary reaction}$$

k_1, k_2 intrinsic second-order rate constants [$\text{M}^{-1}\text{s}^{-1}$].

$$\mathbf{r}_A = -k_1[A][B] \tag{3}$$

$$\mathbf{r}_B = -k_1[A][B]-k_2[R][B] \tag{4}$$

$$\mathbf{r}_R = k_1[A][B]-k_2[R][B] \tag{5}$$

$$\mathbf{r}_S = k_2[R][B] \tag{6}$$

Scheme 2

$$A+B \xrightarrow{k_3} P$$

$$C+B \xrightarrow{k_4} Q$$

k_3, k_4 intrinsic second-order rate constants [$\text{M}^{-1}\text{s}^{-1}$].

$$\mathbf{r}_A = -k_3[A][B] \tag{7}$$

$$\mathbf{r}_B = -k_3[A][B]-k_4[C][B] \tag{8}$$

$$\mathbf{r}_C = -k_4[C][B] \tag{9}$$

$$\mathbf{r}_P = k_3[A][B] \tag{10}$$

$$\mathbf{r}_Q = k_4[C][B] \tag{11}$$

If the solutions of the differential equation systems (2)-(6) and (2), (7)-(11) satisfy certain specified initial and boundary conditions the product distributions can be calculated.

The initial conditions are taken when the eddies are built ($t=0$) assuming that no diffusion and reaction in the eddy have taken place until this moment. If one reactant solution is initially present in the reaction vessel and the second reactant solution is added to it, *i.e.* if the reactions are carried out batch-wise, the initial conditions will depend on the rate of addition of the solutions: If the feed rate is *slow* (*e.g.* dropwise addition), different initial conditions will apply for every new eddy. These initial conditions are determined by the reaction behaviour of the previous eddies. Such a situation is encountered daily in laboratory syntheses. However, for the calculations discussed in the present paper the simplifying assumption is made that the reactant solutions are combined and dispersed *instantaneously* (degree of segregation is one) thus the same initial conditions (see pp. 2930 and 2931) for all eddies apply. If the reactions are conducted under continuous conditions the initial conditions are again different[4]): For instance in the case of competitive, consecutive reactions *(Scheme 1)*, the steady-state initial concentrations of A or R are lower and higher, respectively, than the initial concentrations in batch-wise reactions. Furthermore, these initial conditions will also depend on the degree of dispersion (macroscopic mixing) and thus on the point of entry of the feed streams.

Boundary conditions result from the symmetry of the spherical eddy: There is no flux of the mobile species through the centre of the eddy, *i.e.* the concentration gradient there is zero.

$$\left(\frac{\partial[i]}{\partial \mathrm{r}}\right)_{\mathrm{r}=0}=0. \tag{12}$$

Further boundary conditions are derived from a material balance of the mobile reactants over the solution and the eddy.

$$\mathrm{V_s}\left(\frac{\partial[i]}{\partial \mathrm{t}}\right)_{\mathrm{r}\geqslant\bar{\mathrm{R}}}=-\mathrm{S_e}\mathrm{D_i}\left(\frac{\partial[i]}{\partial \mathrm{r}}\right)_{\mathrm{r}=\bar{\mathrm{R}}}. \tag{13}$$

$\mathrm{V_s}$ volume of solution excluding eddy volume [cm^3];
$\bar{\mathrm{R}}$ mean radius of the eddies [cm];
$\mathrm{S_e}$ surface of the spherical eddy [cm^2].

The left hand side of equation (13) expresses the change in the amount of species i in the volume of solution with respect to time. The right hand side describes the flux of species i through the interface of the substrate eddy. Equation (13) can be rearranged to equation (14).

$$\left(\frac{\partial[i]}{\partial \mathrm{t}}\right)_{\mathrm{r}\geqslant\bar{\mathrm{R}}}=-3\frac{\mathrm{V_e}}{\mathrm{V_s}}\frac{\mathrm{D_i}}{\bar{\mathrm{R}}}\left(\frac{\partial[i]}{\partial \mathrm{r}}\right)_{\mathrm{r}=\bar{\mathrm{R}}}. \tag{14}$$

$\mathrm{V_e}$ volume of the spherical eddy [cm^3].

Equation (2) and the appropriate initial and boundary conditions can be normalized for $i=A, B, C, R$ by introducing the following dimensionless expressions[5]) (the same diffusion coefficient D for all species i is assumed):

$$\boldsymbol{X}=\frac{\mathrm{r}}{\bar{\mathrm{R}}};\quad \boldsymbol{T}=\frac{\mathrm{Dt}}{\bar{\mathrm{R}}^2};\quad \boldsymbol{A}_{\mathrm{A}}=\frac{[A]}{[A]_0};\quad \boldsymbol{B}_{\mathrm{B}}=\frac{[B]}{[B]_0};$$

$$\boldsymbol{\Gamma}_{\mathrm{C}}=\frac{[C]}{[C]_0};\quad \boldsymbol{\Omega}_{\mathrm{A}}=\frac{[R]}{[A]_0};\quad \boldsymbol{E}=\frac{[A]_0}{[B]_0};\quad \boldsymbol{M}=\frac{[C]_0}{[A]_0};\quad \boldsymbol{\alpha}=\frac{\mathrm{V_A}}{\mathrm{V_B}};$$

$$\varphi^2_{\mathrm{B},1}=\frac{\bar{\mathrm{R}}^2k_1[B]_0}{\mathrm{D}};\quad \varphi^2_{\mathrm{B},2}=\frac{\bar{\mathrm{R}}^2k_2[B]_0}{\mathrm{D}};$$

$$\varphi^2_{\mathrm{B},3}=\frac{\bar{\mathrm{R}}^2k_3[B]_0}{\mathrm{D}};\quad \varphi^2_{\mathrm{B},4}=\frac{\bar{\mathrm{R}}^2k_4[B]_0}{\mathrm{D}}.$$

$\mathrm{V_A}$, $\mathrm{V_B}$ volume of solution of reactant A and B, respectively [1].

For the competitive, consecutive and the competitive, parallel reactions this normalization leads to the generalized differential equations (15)-(17) and (18)-(20), respectively.

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[4]) A comprehensive discussion is in preparation.

[5]) The index 0 refers to the initial concentrations before mixing. The normalization using $[A]_0$ or $[B]_0$ leads to dimensionless expressions which are labelled with the index A and B, respectively.

The equations of continuity for the products *S* (competitive, consecutive case), and *P* and *Q* (competitive, parallel case) are redundant as long as it is assumed that the concentration profiles of these species have no influence on the product distribution of the diffusion-reaction process. The total amount of the products *S*, *P* and *Q* can be calculated by a material balance over the whole system.

The term for the diffusional flux in these equations can be neglected if the species *i* is considered to be immobile: In version I [1] zero diffusion was assumed of the molecules *A*, *R* and *S* in the competitive, consecutive case *(Scheme 1)* and of the molecules *A*, *C*, *P* and *Q* in the competitive, parallel case *(Scheme 2)*. These molecules were assumed to be fixed (immobile) within the eddy into which the species *B* diffuse and react. Consequently for version I, the term for the diffusional flux has only to be considered in equations (16) and (19).

In version II the opposite assumption is made, namely that the reagent *B* is fixed within the eddy. The diffusing species are now *A*, *R* and *S* in the consecutive case *(Scheme 1)* and *A*, *C*, *P* and *Q* in the parallel case *(Scheme 2)*. Therefore, for version II the term for the diffusional flux in equations (16) and (19) can be neglected.

The appropriate initial and boundary conditions are given for the competitive, consecutive case after equations (15)-(17) and for the competitive, parallel case after equations (18)-(20).

Competitive, Consecutive Second-Order Reactions *(Scheme 1):*

$$\frac{\partial \boldsymbol{A}_\mathrm{A}}{\partial \boldsymbol{T}} = \frac{\partial^2 \boldsymbol{A}_\mathrm{A}}{\partial \boldsymbol{X}^2} + \frac{2}{\boldsymbol{X}}\frac{\partial \boldsymbol{A}_\mathrm{A}}{\partial \boldsymbol{X}} - \varphi^2_{\mathrm{B},1}\boldsymbol{A}_\mathrm{A}\boldsymbol{B}_\mathrm{B} \tag{15}$$

$$\frac{\partial \boldsymbol{B}_\mathrm{B}}{\partial \boldsymbol{T}} = \frac{\partial^2 \boldsymbol{B}_\mathrm{B}}{\partial \boldsymbol{X}^2} + \frac{2}{\boldsymbol{X}}\frac{\partial \boldsymbol{B}_\mathrm{B}}{\partial \boldsymbol{X}} - \boldsymbol{E}\,\boldsymbol{B}_\mathrm{B}(\varphi^2_{\mathrm{B},1}\boldsymbol{A}_\mathrm{A} + \varphi^2_{\mathrm{B},2}\boldsymbol{\Omega}_\mathrm{A}) \tag{16}$$

$$\frac{\partial \boldsymbol{\Omega}_\mathrm{A}}{\partial \boldsymbol{T}} = \frac{\partial^2 \boldsymbol{\Omega}_\mathrm{A}}{\partial \boldsymbol{X}^2} + \frac{2}{\boldsymbol{X}}\frac{\partial \boldsymbol{\Omega}_\mathrm{A}}{\partial \boldsymbol{X}} + \boldsymbol{B}_\mathrm{B}(\varphi^2_{\mathrm{B},1}\boldsymbol{A}_\mathrm{A} - \varphi^2_{\mathrm{B},2}\boldsymbol{\Omega}_\mathrm{A}) \tag{17}$$

Initial conditions: $\boldsymbol{T} = 0$

Version I: $\boldsymbol{X} < 1$: $\boldsymbol{A}_\mathrm{A} = 1$; $\boldsymbol{B}_\mathrm{B} = 0$; $\boldsymbol{\Omega}_\mathrm{A} = 0$
$\boldsymbol{X} = 1$: $\boldsymbol{A}_\mathrm{A} = 1$; $\boldsymbol{B}_\mathrm{B} = 1$; $\boldsymbol{\Omega}_\mathrm{A} = 0$

Version II: $\boldsymbol{X} < 1$: $\boldsymbol{A}_\mathrm{A} = 0$; $\boldsymbol{B}_\mathrm{B} = 1$; $\boldsymbol{\Omega}_\mathrm{A} = 0$
$\boldsymbol{X} = 1$: $\boldsymbol{A}_\mathrm{A} = 1$; $\boldsymbol{B}_\mathrm{B} = 1$; $\boldsymbol{\Omega}_\mathrm{A} = 0$

Boundary conditions: $\boldsymbol{T} > 0$

Version I: $\boldsymbol{X} = 0$: $\dfrac{\partial \boldsymbol{B}_\mathrm{B}}{\partial \boldsymbol{X}} = 0$

$\boldsymbol{X} = 1$: $\dfrac{\partial \boldsymbol{B}_\mathrm{B}}{\partial \boldsymbol{T}} = -3\alpha\dfrac{\partial \boldsymbol{B}_\mathrm{B}}{\partial \boldsymbol{X}}$

Version II:

$$X=0:\quad \frac{\partial A_A}{\partial X}=0;\qquad \frac{\partial \Omega_A}{\partial X}=0$$

$$X=1:\quad \frac{\partial A_A}{\partial T}=-\frac{3}{\alpha}\frac{\partial A_A}{\partial X};\qquad \frac{\partial \Omega_A}{\partial T}=-\frac{3}{\alpha}\frac{\partial \Omega_A}{\partial X}$$

Competitive, Parallel Second-Order Reactions *(Scheme 2):*

$$\frac{\partial A_A}{\partial T}=\frac{\partial^2 A_A}{\partial X^2}+\frac{2}{X}\frac{\partial A_A}{\partial X}-\varphi^2_{B,3}A_A B_B \tag{18}$$

$$\frac{\partial B_B}{\partial T}=\frac{\partial^2 B_B}{\partial X^2}+\frac{2}{X}\frac{\partial B_B}{\partial X}-E\,B_B(\varphi^2_{B,3}A_A+\varphi^2_{B,4}\Gamma_C M) \tag{19}$$

$$\frac{\partial \Gamma_C}{\partial T}=\frac{\partial^2 \Gamma_C}{\partial X^2}+\frac{2}{X}\frac{\partial \Gamma_C}{\partial X}-\varphi^2_{B,4}\Gamma_C B_B \tag{20}$$

Initial conditions: $T=0$

Version I:

$X<1:\quad A_A=1;\quad B_B=0;\quad \Gamma_C=1$
$X=1:\quad A_A=1;\quad B_B=1;\quad \Gamma_C=1$

Version II:

$X<1:\quad A_A=0;\quad B_B=1;\quad \Gamma_C=0$
$X=1:\quad A_A=1;\quad B_B=1;\quad \Gamma_C=1$

Boundary conditions: $T>0$

Version I:

$$X=0:\quad \frac{\partial B_B}{\partial X}=0$$

$$X=1:\quad \frac{\partial B_B}{\partial T}=-3\alpha\frac{\partial B_B}{\partial X}$$

Version II:

$$X=0:\quad \frac{\partial A_A}{\partial X}=0;\qquad \frac{\partial \Gamma_C}{\partial X}=0$$

$$X=1:\quad \frac{\partial A_A}{\partial T}=-\frac{3}{\alpha}\frac{\partial A_A}{\partial X};\qquad \frac{\partial \Gamma_C}{\partial T}=-\frac{3}{\alpha}\frac{\partial \Gamma_C}{\partial X}$$

3. Procedure for Numerical Solution. - Since an analytical solution of the two systems of equation (15)-(17) and (18)-(20) does not exist, a numerical approximation must be used. In addition to the stable explicit finite difference method [5], the *Method of Lines* [6] was employed. When $\varphi^2_{B,j} < 10^4$, the algorithm of *Runge-Kutta-Gill* was used for the integration. For values of $\varphi^2_{B,j} > 10^4$ the method of *Hindemarsch & Gear* [7] for stiff differential equations was applied.

4. Simulated Behaviour of Mixing Disguised Reactions. - The selectivity behaviour of mixing-disguised competitive, consecutive and competitive, parallel reactions are shown in *Figure 1* and *2* and *Figures 3-5*, respectively. The dotted and the solid lines represent the behaviour calculated using version I and version II, respectively. The appropriate values are listed in *Tables 1* and *2*. The product

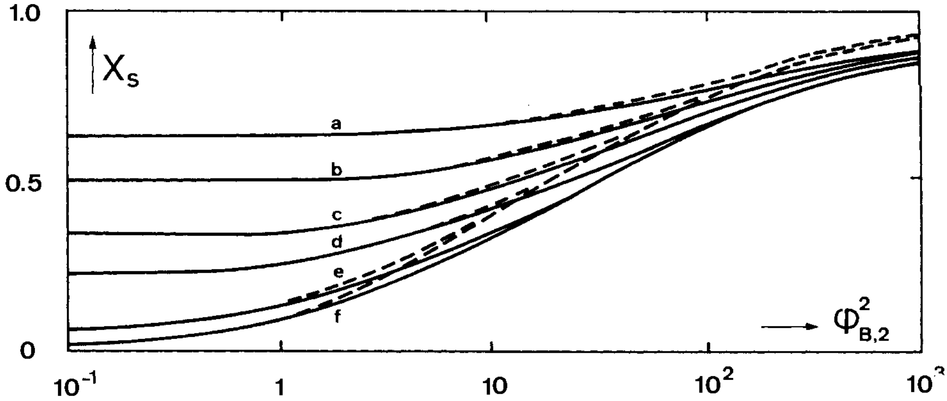

Fig. 1. *Competitive, consecutive second-order reactions* (Scheme 1): *Calculated relative yields* X_S *as a function of* $\varphi^2_{B,2}$ *for different* (a-f) *intrinsic selectivities* $\varphi^2_{B,1}/\varphi^2_{B,2}$ (spherical geometry)
a = 1; b = 2; c = 5; d = 10; e = 10^2; f = 10^4; *E* = 1; α = 1
------ Version I; ——— Version II

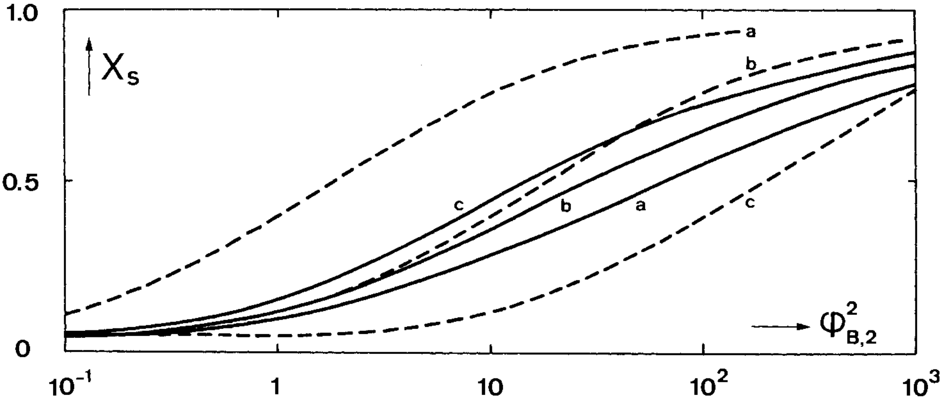

Fig. 2. *Competitive, consecutive second-order reactions* (Scheme 1): *Calculated relative yields* X_S *as a function of* $\varphi^2_{B,2}$ *for different* (a-c) *values of* α (spherical geometry)
a = 0.1; b = 1.0; c = 10; *E* α = 1; $\varphi^2_{B,1}/\varphi^2_{B,2}$ = 100
------ Version I; ——— Version II

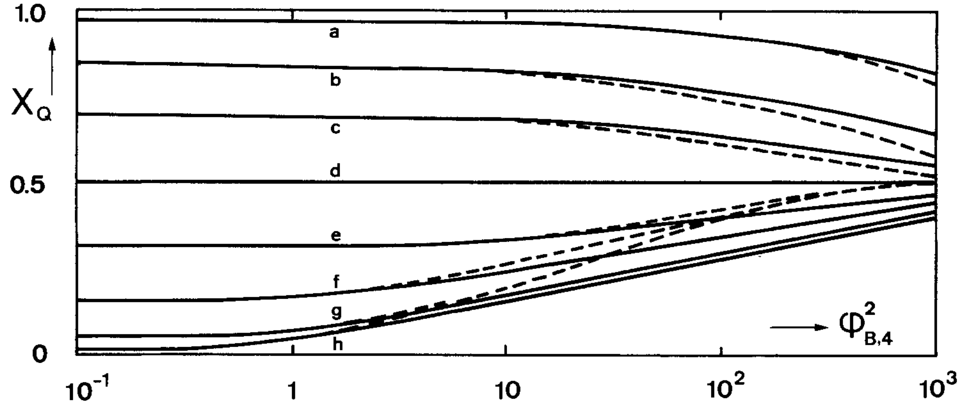

Fig. 3. *Competitive, parallel second-order reactions* (Scheme 2): *Calculated relative yields X_Q as a function of $\varphi^2_{B,4}$ for different* (a-h) *intrinsic selectivities* $\varphi^2_{B,3}/\varphi^2_{B,4}$ (spherical geometry)
a=0.01; b=0.1; c=0.3; d=1; e=3; f=10; g=10^2; h=10^4; $E=1$; $M=1$; $\alpha=1$
------ Version I; ——— Version II

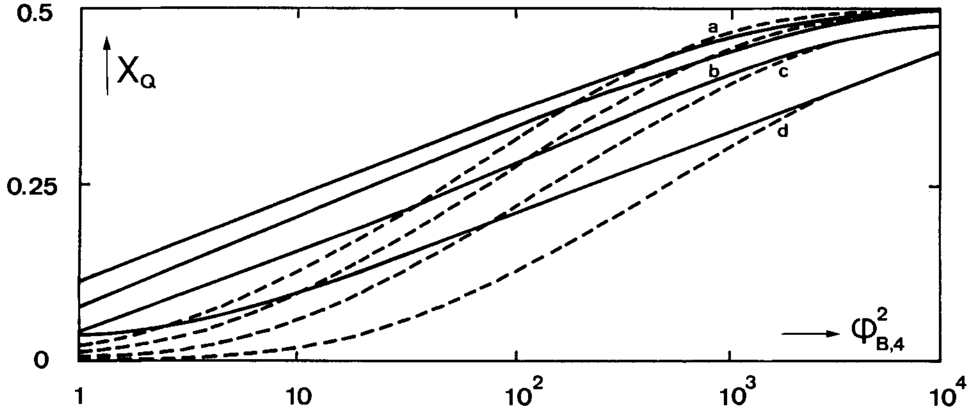

Fig. 4. *Competitive, parallel second-order reactions* (Scheme 2): *Calculated relative yields X_Q as a function of $\varphi^2_{B,4}$ for different* (a-d) *values of E* (spherical geometry)
a=1; b=2; c=5; d=10; $\varphi^2_{B,3}/\varphi^2_{B,4}=100$; $M=1$; $\alpha=1$
------ Version I; ——— Version II

distribution after 100% conversion is expressed by the relative yield X_S or X_Q. It is defined as the fraction of the reagent *B* which has reacted after 100% conversion to the product *S* or *Q*. The results in *Figures 1-5* are self-explanatory[6]).

The general behaviour of the mixing-disguised reactions has already been discussed in detail [1]. However, there are two major differences between the predicted behaviour calculated according to version I and that calculated according to version II: First, different slopes of the selectivity curves are observed *(Figures 1-4)*. The selectivity curves for version I always have a greater slope than those for version II. Second, there is a striking difference in the dependence of X_S or X_Q on the volume ratio α. These differences can be explained by the different

[6]) Additional calculations can be found in [8] and [9].

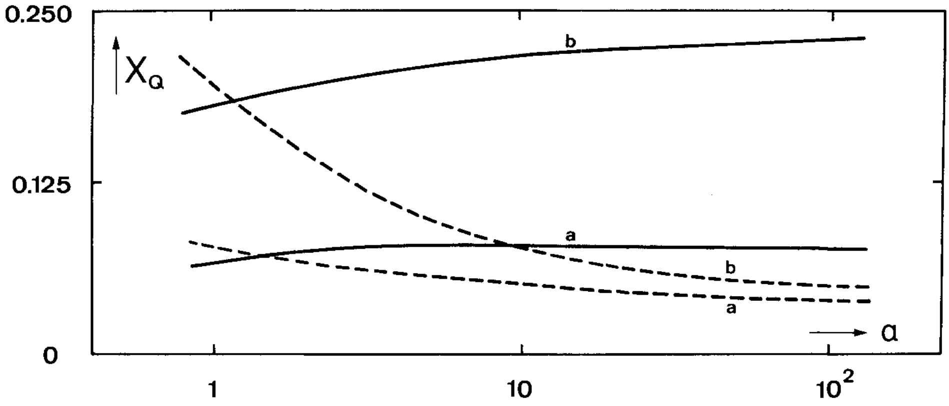

Fig. 5. *Competitive, parallel second-order reactions* (Scheme 2): *Calculated relative yields X_Q as a function of* α *for different* (a,b) *values of* $\varphi^2_{B,4}$ (spherical geometry)
a = 1; b = 10; $\varphi^2_{B,3}/\varphi^2_{B,4} = 100$; E $\alpha = 1$; $M = 1$
------ Version I; ——— Version II

Table 1. *Calculated relative yields X_S as a function of* $\varphi^2_{B,1}$, $\varphi^2_{B,2}$, E *and* α *for a competitive, consecutive second-order reaction* (Scheme 1; spherical geometry)
X_S-values calculated according to version II (For X_S-values according to version I, see [1])
RC: reaction-controlled

$\varphi^2_{B,1}/\varphi^2_{B,2}$	$\varphi^2_{B,2}$	E	α	X_S	$\varphi^2_{B,1}/\varphi^2_{B,2}$	$\varphi^2_{B,2}$	E	α	X_S
1	RC	1	1	0.636	100	250	1	1	0.743
	4			0.646		1000			0.842
	10			0.662	10000	RC	1	1	0.002
	40			0.718		0.1			0.002
	100			0.772		0.4			0.005
	1000			0.887		1			0.100
10	RC	1	1	0.232		4			0.220
	1			0.252	100	0.1	10	0.1	0.053
	4			0.314		0.4			0.063
	10			0.404		1			0.093
	40			0.569		4			0.187
	100			0.655		10			0.277
	400			0.748		40			0.441
	1000			0.814		100			0.552
100	RC	1	1	0.052		1000			0.780
	0.1			0.056	100	0.1	0.1	10	0.060
	0.25			0.064		0.4			0.092
	1			0.117		1			0.150
	2.5			0.192		4			0.307
	10			0.351		10			0.442
	25			0.480		40			0.632
	100			0.652		100			0.725

Table 2. *Calculated relative yields X_Q as a function of $\varphi^2_{B,3}$, $\varphi^2_{B,4}$, E and α for a competitive, parallel second-order reaction* (Scheme 2; spherical geometry)
X_Q-values calculated according to version II (For X_S-values according to version I, see [1])
M=1; RC: reaction-controlled

$\varphi^2_{B,3}/\varphi^2_{B,4}$	$\varphi^2_{B,4}$	E	α	X_Q	$\varphi^2_{B,3}/\varphi^2_{B,4}$	$\varphi^2_{B,4}$	E	α	X_Q
0.01	RC	1	1	0.97	100	RC	1	1	0.03
	0.1			0.97		0.1			0.04
	1			0.97		1			0.07
	10			0.97		10			0.18
	30			0.97		100			0.31
	100			0.94		1000			0.40
	300			0.89	1000	RC	1	1	0.01
	1000			0.82		0.1			0.01
0.1	RC	1	1	0.84		1			0.05
	0.1			0.84		3			0.10
	1			0.83		10			0.16
	10			0.83		100			0.31
	30			0.81		1000			0.41
	100			0.76	100	RC	2	1	0.01
	1000			0.65		1			0.03
0.3	RC	1	1	0.68		10			0.10
	0.1			0.68		100			0.24
	1			0.68		1000			0.35
	10			0.68		10000			0.45
	100			0.63	100	RC	5	1	0.01
	1000			0.57		1			0.02
1	RC	1	1	0.50		10			0.06
	10			0.50		100			0.17
	1000			0.50		1000			0.30
3	RC	1	1	0.32		10000			0.42
	0.1			0.32	100	RC	10	1	0.01
	1			0.32		1			0.02
	10			0.34		10			0.05
	100			0.41		100			0.15
	1000			0.46		1000			0.25
10	RC	1	1	0.16		10000			0.39
	0.1			0.16	100	1	0.2	5	0.08
	1			0.17		1	0.1	10	0.08
	10			0.24		1	0.01	100	0.08
	100			0.35	100	10	0.2	5	0.21
	1000			0.43		10	0.1	10	0.22
						10	0.01	100	0.23

concentration profiles for both versions. This can be shown, for instance, using the concentration profiles for the competitive, consecutive reactions *(Figure 6):* In version I every product R that is formed remains exposed to further attack by the diffusing reagent B. In contrast, in version II some of species R is allowed to escape from the reaction zone thus decreasing the probability of the second reaction to form S and, therefore, decreasing the slope of the selectivity curves.

5. Conclusions. - The influence of micromixing on the product distribution of mixing-disguised reactions has been simulated with the help of a simple mixing-

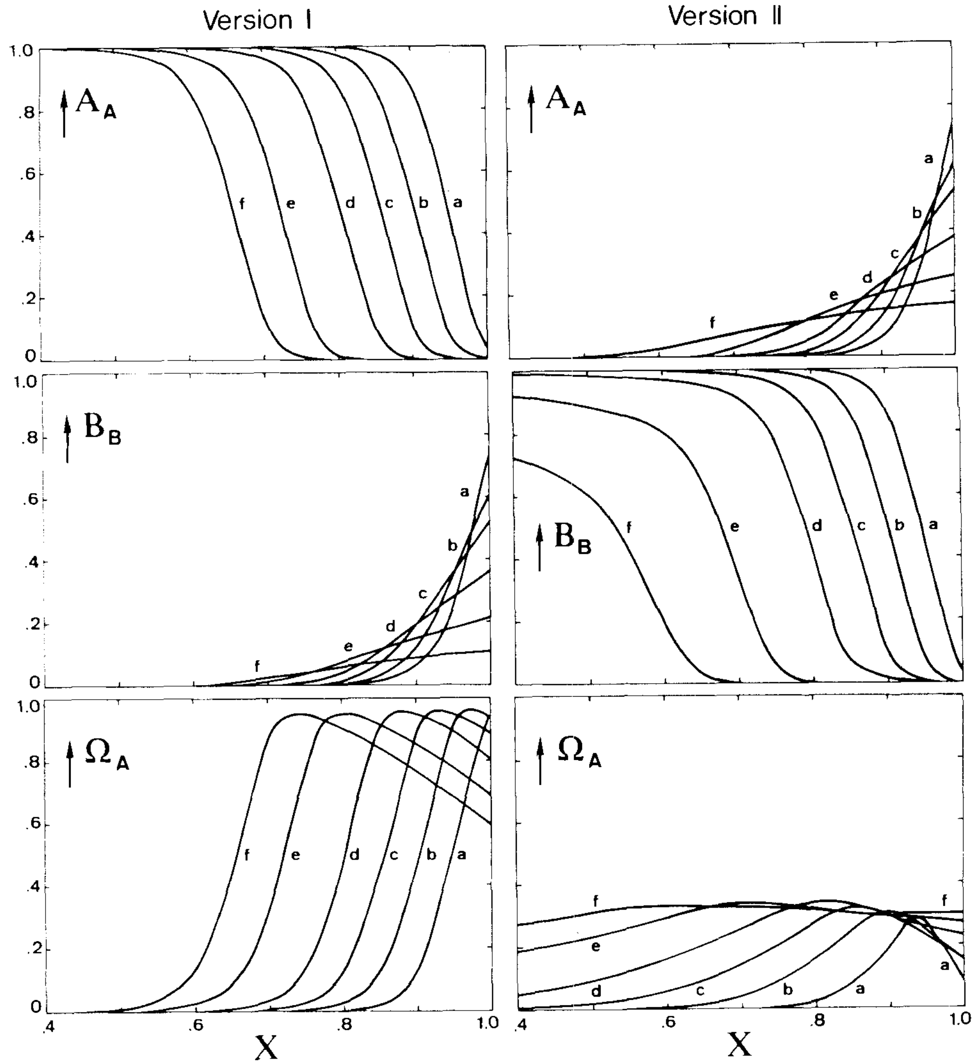

Fig. 6. *Calculated concentration profiles of mixing-disguised competitive, consecutive second-order reactions:*

$\varphi^2_{B,1}/\varphi^2_{B,2} = 1000/10$; $E = 1$; $\alpha = 1$

Reaction times (T): a(0.004); b(0.01); c(0.02); d(0.04); e(0.1); f(0.2)

reaction model. Depending on the basic assumptions used in the calculation of the coupling of mass diffusion with the chemical reactions some differences in the predicted product distributions can be observed. Which of these assumptions are more realistic only future experiments can decide. Despite these minor differences the previous conclusions [1] concerning the usefulness of the moduli $\varphi^2_{B,j}$ as mixing criteria are still valid.

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288. Chemical Selectivities Disguised by Mass Diffusion. IV. Mixing-Disguised Nitrations of Aromatic Compounds with Nitronium Salts[1][2]

4th Communication on the Selectivity of Chemical Processes[1]

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Zum ehrenden Andenken an Prof. Dr. H. Hopff

(24.VIII.77)

Summary

The disguise of the intrinsic selectivity of competitive, consecutive reaction systems by the mixing process is demonstrated experimentally using the fast nitration of a number of aromatic compounds with nitronium salts in nitromethane. The measured product distributions were compared with the distributions predicted from our mixing-reaction model developed previously [2] [4]. This comparison enabled the relative intrinsic rate constants for the second nitration step of the aromatic compounds investigated to be determined.

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[1] Part III and 3rd Communication *cf.* [4].

[2] Results taken from the PhD. thesis of *F. Nabholz* [1].