

CHEMICAL SELECTIVITIES DISGUISED BY MIXING

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Abstract - The disguising of the intrinsic selectivity of competitive reaction systems by the mixing process is demonstrated experimentally using the fast nitrations of a number of aromatic compounds, a fast azo coupling reaction and a fast bromination. A mixing-reaction model is presented 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. The usefulness of this model is demonstrated by comparison of prediction and experiment in the examples used.

INTRODUCTION

The study of the kinetics and the product distribution of a chemical reaction can be used to establish the mechanism of this reaction if, and only if, the results give proper insight into its intrinsic course, namely the bond-making and bond-breaking steps. In the case of fast reactions this condition is not always fulfilled as diffusion effects, due to mixing and encounter processes involving the reactants, can disguise the kinetics of chemical reactions and hence affect the product distribution.

The present lecture will deal with the influence which the rate of mixing might have on the product distribution of reactions in miscible liquid-liquid phase systems.

In spite of much theoretical work which has been published on the subject, mixing processes are far from being clearly understood. A major reason for this could be the insufficient communication between chemical engineers and chemists: On the one hand, there are the chemical engineers who have introduced many models claiming to describe mixing phenomena. However, the chemical reactions which they have used to test these models were incompletely characterised kinetically and mechanistically. On the other hand, there are the chemists having well characterised fast reactions at hand, who have felt unable to apply the often abstract models of the chemical engineers to explain the observed influence of mixing on product distribution.

The aim of my lecture is therefore, to unite the macroscopic view of the chemical engineers with the microscopic molecular way of thinking of the chemists in the hope of stimulating further research on the coupling between mixing and chemical reaction. The study of mixing effects is of importance for two reasons: first, because understanding them creates the possibility of gaining valuable information on the intrinsic course of the bond-making and bond-breaking events, even from measured chemical selectivities which are subject to mixing-disguise and, second, because a knowledge of the influence of mixing on the behaviour of a chemical process is of decisive importance in the control and optimisation of the distribution of the products.

For the sake of clarity, I shall confine the subject of this lecture to single-solvent systems, i.e. to systems where two reactants are separately dissolved in the same solvent and then the resulting solutions are mixed to allow the reaction to occur.

First, I shall present some strange experimental facts. We shall then ask ourselves what happens when two miscible solutions are mixed together and how long it will take until homogeneity of the resulting reaction mixture is reached. In order to answer these questions we shall develop a simple mixing -model which will finally help us to explain most of the strange experimental results.

SOME STRANGE EXPERIMENTAL RESULTS

These results are exemplified by the following 3 typical instances:

a) In many studies the remarkable observation has been reported that in an equimolar nitration of durene (1,2,4,5-tetramethylbenzene) mainly dinitrodurene and unchanged durene were found, but hardly any mononitrodurene (Refs. 1-4). Similar observations have been made with other substrates (Refs. 5 and 6). These experimental results are in apparent contradiction of the mechanism of electrophilic aromatic substitution, according to which the second nitration should be slower than the first by a factor of at least 10 to 100 because of the deactivating effect of the first nitro group. Some authors sought to explain the apparently faster second nitration by reaction mechanistic considerations (Refs. 7 and 8). Many other authors, however, pointed to mixing effects as the possible cause (Refs. 2-4,6,9-11).

b) The coupling reaction of a diazonium ion with an excess of a bifunctional coupling component often yields not only a mixture of the o- and p-monoazo compounds but also appreciable amounts of the bisazo product (Refs. 12-14). For a synthetic chemist it is surprising to learn that the final relative product ratio of the mono- to the bisazo compound varies with the stirring rate. At high stirring rates the undesired by-product namely the bisazo compound, vanishes.

c) In the bromination of resorcinol with bromine in methanol, mono-, di- and tri-bromoresorcinols are formed. The ratio of the 2,4- and 4,6-dibromo isomers is strongly dependent on the stirring rate even under conditions where mainly dibromo compounds are formed.

PARTIAL PROCESSES IN A CHEMICAL REACTION

In order to understand these unusual experimental results, it has proved very useful to subdivide the whole liquid-liquid reaction system into various partial processes (Fig. 1):

Let us start with two separate solutions, one containing the reactant A and the other containing the reactant B. When the two solutions are united, and if turbulent flow is generated, e.g. by mechanical stirring, there is bulk motion of small liquid elements. These groups of molecules are called eddies, and their bulk motion is called eddy diffusion or dispersion (first process in Fig. 1). The average size of these eddies, the so-called "segregation length of the mixture", depends on the turbulence which is produced. It can be estimated, e.g. with the help of the turbulence theory of Kolmogoroff (Refs. 15,16, and 17), to be of the order of 10^{-2} to 10^{-3} cm in diameter.

In general, the mean size of these eddies increases with increasing viscosity of the reaction medium. There are, however, practical limits to a further subdivision of the eddies by e.g. increasing the stirring rate. These limits are set by the energy uptake of the mixing system. The size of the eddies is thought to be inversely proportional to only the 4th root of the stirring energy taken up and should be associated with the smallest of the energy containing eddies (Ref. 16).

The process of dispersion leads to a macroscopic homogeneity of the reaction mixture. In this state further mixing takes place, but now mainly by molecular diffusion (second process in Fig. 1). The two mixing processes do not strictly occur consecutively but simultaneously. Following a suggestion of Brodkey (Ref. 17), this can be visualised as shown in Fig. 2: going from left to right, the scale of segregation is reduced by the process of dispersion. The superimposed effect of molecular diffusion characterised by the intensity

of segregation is illustrated by the columns.

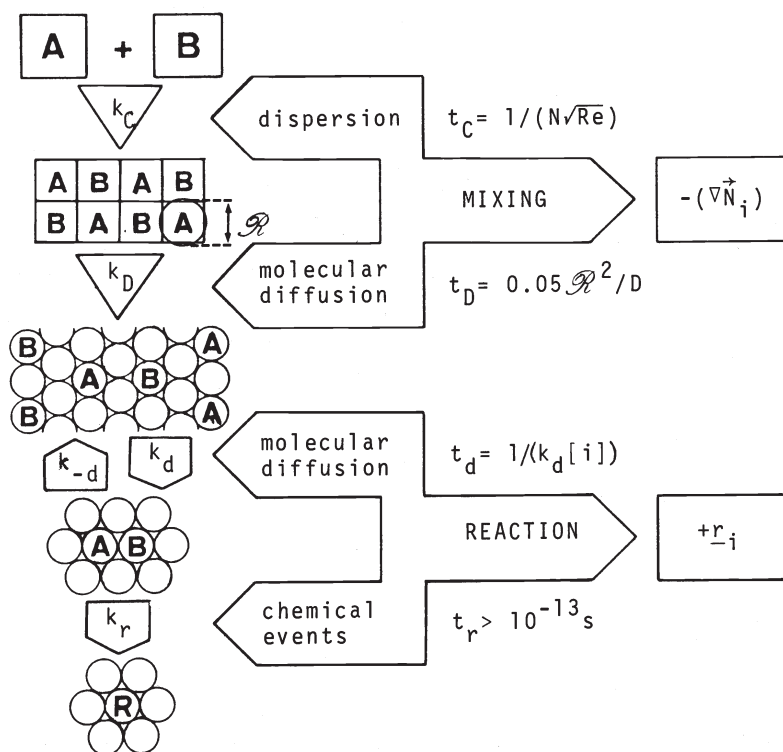


Fig. 1. Partial processes in a chemical reaction.

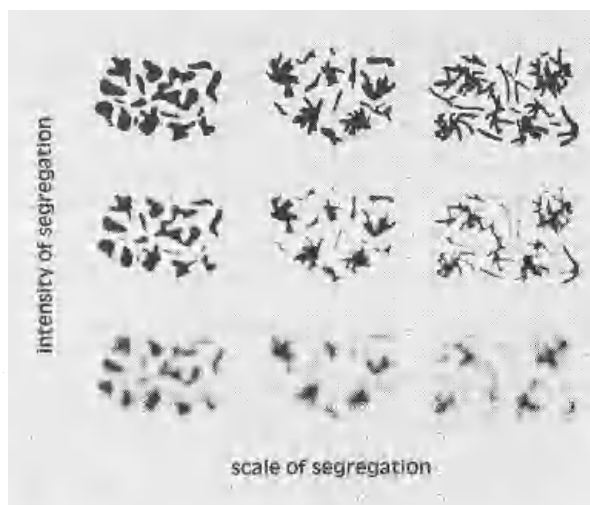


Fig. 2. Mechanism of mixing (Ref. 17).

During (for fast reactions) or after (for slow reactions) these mixing processes the chemical reaction sets in to a significant extent. This can only take place when molecular diffusion of each reactant brings it into contact with the other, i.e. when the reactants encounter each other to form the encounter pair. Only at this stage can the chemical events occur.

The relative rates and the relaxation times of these various partial processes will be dependent on the reaction conditions and also on the size of the reaction vessel. They can all be estimated using the equations given in Fig. 1.

For a situation which is typical for laboratory equipment, i.e. for a situation that the experimental chemist meets daily in the laboratory, the following characteristic relaxation times can be estimated: the relaxation time t_c of the convective mixing, the dispersion, is of the order of $10^{-3} \dots 10^{-4}$ s. For the estimation of the relaxation time t_D of the micromixing process, i.e. of the molecular diffusion into and out of the eddies, spherical eddies are assumed. With the help of the turbulence theory of Kolmogoroff (Ref. 16) their average radius can be calculated according to equation (1).

$$\mathcal{R} = \ell_G \text{Re}^{-3/4} \quad (1)$$

with $\mathcal{R}$: average eddy radius (half of the Kolmogoroff diameter)
 ℓ_G : characteristic size of the macrosystem. For a stirred reaction system: ℓ_G = radius of the impeller
 Re: Reynolds number. For stirred reaction system:

$$\text{Re} = N \ell_G^2 / \nu \quad (2)$$

N : rate of stirring
 ν : kinematic viscosity

Using typical values for the diffusion coefficient D leads us to $t_D = 10^{-1} \dots 10^{-2}$ s. The relaxation time t_d of the encounter process depends on the concentration of the reactants and on the value of $k_d = 4\pi N_A(D_A + D_B)\rho^*$, where N_A is the Avogadro number, D_A and D_B are the diffusion coefficients of the reactants A and B, respectively, and ρ^* is the encounter distance which depends on the potential energy of the reactants (Ref. 18). In the absence of intermolecular coulombic forces and for a concentration of $10^{-1} \dots 10^{-2}$ mol·dm⁻³ for the reactant which is in excess, t_d can be estimated to be of the order of $10^{-7} \dots 10^{-8}$ s. The relaxation time t_r of the chemical events can take all values greater than 10^{-13} s. It is obvious that the slowest, non-chemical partial process is the mixing by molecular diffusion. Hence if a chemical event occurs faster than this diffusion process, the product distribution of a competitive reaction may be influenced by the rate of mixing.

THE MIXING-REACTION MODEL MIRE

Figure 3 helps to give a qualitative understanding of the influence of the micromixing on the product distribution in a competitive consecutive reaction.

Let us assume that the steps of the described reaction are each first order in A and B for the first step, and in R and B for the second step, respectively. Furthermore, let us assume, that the rate constant k_1 is larger than k_2 , and that 1 equivalent of A and 1 equivalent of B are allowed to react.

Schematically, the following two extreme cases are illustrated:

(a) $t_D \ll t_r$. The relaxation time t_D for the micromixing is much smaller than the relaxation time t_r for the reaction (encounter process + chemical events). After the solutions of A and B have been united, the micromixing between the two liquid elements occurs and finishes before any chemical reaction has taken place to a significant extent. During the reaction, as would be expected from the fact that k_1 is greater than k_2 , more primary product R than secondary product S will be formed.

(b) $t_D \gg t_r$. The chemical reaction is much faster than the micromixing. After a first time interval, after the solutions have been united, A and B will have reacted at the boundary zone of the eddies to give the primary product R. In a further time interval a molecule B can react with a further molecule A to form R only if it succeeds in diffusing through the boundary zone of R molecules already formed without being trapped there by the substance R to give the secondary product S. Whether or not it succeeds in doing this will mainly depend on the ratio of the diffusion rate to the reaction rate of the second reaction step. In the extreme case, a mixing-controlled reaction will convert all the R into S before the molecule B finds a further molecule A. Thus, at the end of the reaction practically only the secondary product S will be present and no primary product R can be detected. In this case the selectivity k_1/k_2 loses its influence on the product distribution.

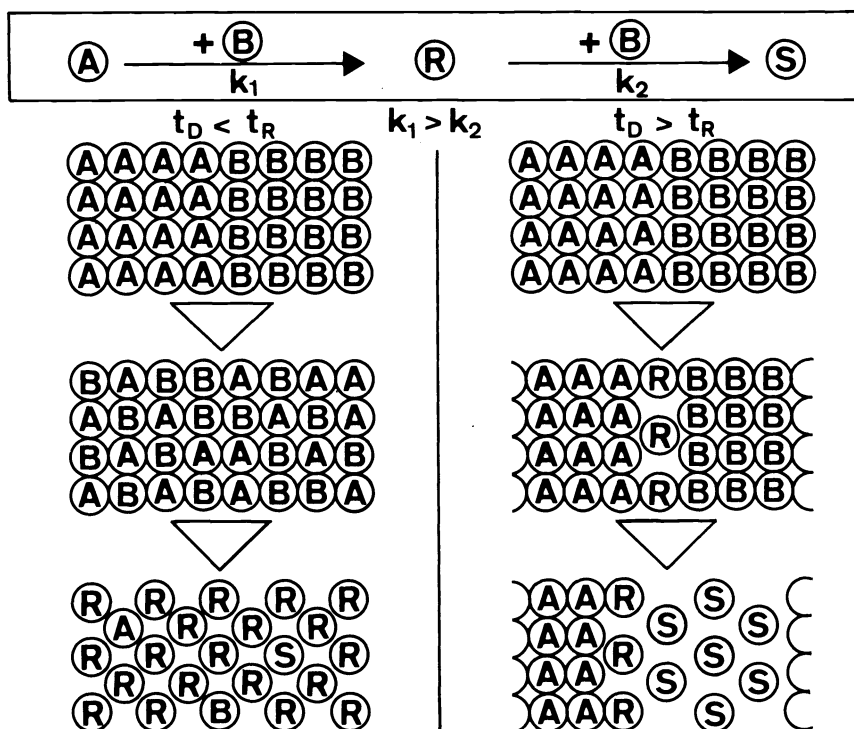


Fig. 3. A qualitative description of the influence of the micromixing on the product distribution in a competitive consecutive reaction.

For the quantitative description of such micromixing effects a simple mixing-reaction model (MIRE) has been developed and described in great detail elsewhere (Ref. 19). Here, only a short summary of the most important features of the MIRE model is given to enable a significant comparison of the calculated with the experimentally measured behaviour of reaction systems which are subject to mixing-disguise.

The basis for the quantitative description is the equation of continuity (3):

$$\frac{\partial [i]}{\partial t} = - (\nabla \vec{N}_i) + \underline{r}_i \quad (3)$$

where

- $[i]$: concentration of the component i
- ∇ : "del" or "nabla" operator
- $\vec{N}_i$: flux vector of the component i
- t : time
- $\underline{r}_i$: rate of formation of the component i

It is assumed that the net effect of the continually shifting interfaces between liquid elements resulting from the turbulent action, is the same as if an individual liquid element, an eddy, of a given concentration of one reactant were suspended in a fluid of suitably average concentration of the other reactant. This eddy is then chosen as the diffusion-reaction system.

As the reactions considered occur in dilute solution the following simplifications are justified:

the diffusion coefficients are constant and the same for all species ($D_i = D$);

the total molar concentration remains constant;

the molar average velocity of the solution within the eddy is zero;

the diffusion and reaction occur isothermally, because the thermal diffusivity is some two orders of magnitude greater than the mass diffusivity.

With the help of these simplifications, and arbitrarily assuming the shape of the eddy to be spherical, the radius $\mathcal{R}$ being constant with time, the concentration of the component i at time t and radius r ($r \leq \mathcal{R}$) follows.

$$\frac{\partial[i]}{\partial t} = D \left(\frac{\partial^2[i]}{\partial r^2} + \frac{2}{r} \frac{\partial[i]}{\partial r} \right) + \underline{r}_i \quad (4)$$

where D : diffusion coefficient
 r : polar coordinate

For one of the commonest reaction system, namely for competitive consecutive second-order reactions as shown in Fig. 3, the molar rate of formation $\underline{r}_i$ for every component i involved is given by the following equations (5)-(8).

$$\underline{r}_A = -k_1[A][B] \quad (5)$$

$$\underline{r}_B = -k_1[A][B] - k_2[R][B] \quad (6)$$

$$\underline{r}_R = k_1[A][B] - k_2[R][B] \quad (7)$$

$$\underline{r}_S = k_2[R][B] \quad (8)$$

For calculating the reaction behaviour and the product distribution of this mixing-reaction system (4)-(8) the initial and the boundary conditions must be specified. They differ considerably, depending on whether the reaction is carried out batchwise or continuously. For given initial and boundary conditions the final (100% conversion) product distribution observed in second-order competitive consecutive reactions, influenced by the mixing rate, is unambiguously determined by the four quantities E , α , $\phi_{B,1}^2$ and $\phi_{B,2}^2$ (Ref. 19) and, if the reaction is carried out continuously, by an additional parameter γ which connects the macroscopic steady-state of the continuously operated reaction vessel with the non steady-state reaction behaviour within a single eddy.

$$E = \frac{[A]_0}{[B]_0}; \alpha = \frac{V_A}{V_B}; \gamma = \frac{\tau_V}{\tau_E}; \phi_{B,1}^2 = \frac{\mathcal{R}^2 k_1 [B]_0}{D}; \phi_{B,2}^2 = \frac{\mathcal{R}^2 k_2 [B]_0}{D}$$

E is the ratio of the initial concentrations of the reactants A and B before the reactant solutions have been united, α is the volume ratio of the reactant solutions of A and B to be mixed, γ is the ratio of the mean residence time τ_V and the lifetime τ_E of the eddy. The ϕ^2 values are proportional to the ratio of the relaxation times of the micromixing process t_D and the chemical reaction t_R . They show how strongly a step in the chemical reaction is hindered by preceding micromixing. The extent to which this hindrance by molecular diffusion influences also the product distribution is illustrated in Fig. 4, where the relative yield X_S , calculated using the MIRE model (Ref. 19), is plotted against the mixing modul $\phi_{B,2}^2$.

The relative yield X_S is defined (9) as the fraction of B molecules that has reacted to give S after 100% conversion.

$$X_S = \frac{2(S)_\infty}{(R)_\infty + 2(S)_\infty} \quad (9)$$

Here $(R)_\infty$ and $(S)_\infty$ are the total amounts of R and S formed after infinite time.

The MIRE calculations show for batchwise (Ref. 19) as well as for continuous operation (Ref. 20) what was already expected according to the qualitative description in Fig. 3. The smaller $\phi_{B,2}^2$, the closer the relative yields X_S of

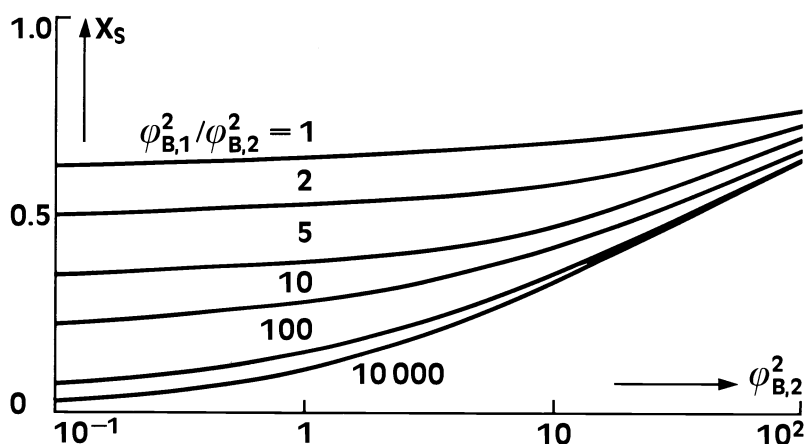


Fig. 4. Calculated relative yields X_S as a function of the mixing modulus $\phi_{B,2}^2$ for several intrinsic selectivities $\phi_{B,1}^2/\phi_{B,2}^2$. Assumptions: competitive consecutive second-order reaction; batchwise operation; spherical eddy; $E = 1$; $\alpha = 1$.

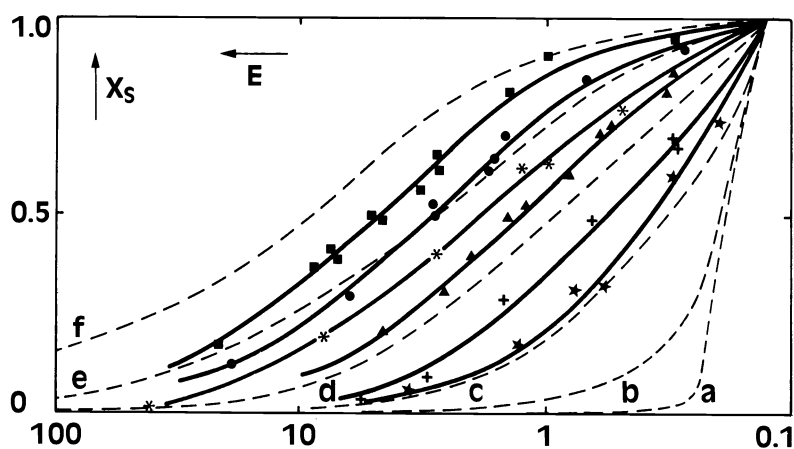


Fig. 5. Mixing-disguised nitration of aromatic compounds (A) by NO_2PF_6 (B) in nitromethane (20°C) (Ref. 21). $\alpha = 4$. Experimental results: $\star$ p-xylene; $+$ m-xylene; $\blacktriangle$ mesitylene = 1,3,5-trimethylbenzene; $*$ isodurene; $\bullet$ durene = 1,2,4,5-tetramethylbenzene; $\blacksquare$ prehnitene = 1,2,3,4-tetramethylbenzene. Calculated curves (broken curves) for several (a-f) values of $E\phi_{B,2}^2$ (a $\ll 1$, reaction-controlled; b = 1; c = 10; d = 10^2 ; e = 10^3 ; f = 10^4). $\phi_{B,1}^2/\phi_{B,2}^2 \geq 100$.

the secondary product S will approach the values for the reaction-controlled case (in Fig. 3: $t_D \ll t_R$). As the $\phi_{B,2}^2$ values increase, X_S becomes increasingly strongly disguised by diffusion effects and approaches the value of 1. The more marked this disguise by mixing, the smaller the influence of the intrinsic selectivity $\phi_{B,1}^2/\phi_{B,2}^2$ (or k_1/k_2) on the product distribution becomes (in Fig. 3: $t_D \gg t_R$). If the intrinsic selectivity exceeds about 100, then the product distribution and thus the relative yield X_S are almost wholly determined by the $\phi_{B,2}^2$ values; this is true for $E = 1$, $\alpha = 1$, and for batchwise operation if the reactant solutions are united instantaneously. Under different reaction conditions similar limiting values for the intrinsic selectivity exist at which X_S becomes mainly determined by $\phi_{B,2}^2$.

MODEL-EXPERIMENT COMPARISONS

Having discussed a simple mixing-reaction model (MIRE model), let us return to the peculiar experimental results mentioned at the beginning of this lecture. Fig. 5 summarizes a number of experimental results of the consecutive nitration of several aromatic compounds with nitronium hexafluorophosphate in nitromethane. The general characteristics of this nitrating systems have been reported elsewhere (Ref. 4 and 21). The experimental results are compared with the predicted curves calculated according to the mixing-reaction model. The relative yields X_S of the dinitro products S are plotted against E . The resulting selectivity curves all lie on S-shaped curves whose positions along the E -axis depend, for a given α and a given ratio of $\phi_{B,1}^2/\phi_{B,2}^2$ (i.e. k_1/k_2) only on the values of $E\phi_{B,2}^2$. Numerous model calculations as well as the calculated curves in Fig. 3 show, that for $\phi_{B,1}^2/\phi_{B,2}^2 \geq 100$ and a given α , these positions are essentially determined only by the values of $E\phi_{B,2}^2$. Under identical experimental conditions, the relative k_2 -values for different aromatic substrates can be found from the relative positions of the respective selectivity curves. If one of the intrinsic k_2 -values can be measured experimentally, e.g. in a rapid mixing chamber, the others can be calculated from the relative k_2 -values. With the help of this method the intrinsic k_2 -values of the five aromatic compounds p-xylene, m-xylene, mesitylene, isodurene, durene and prehnitene were evaluated by measuring the k_2 -value of mesitylene (Ref. 21). In Fig. 6 these values are compared with the corresponding k_2 -values determined by nitration experiments in mixed acid (Ref.22).

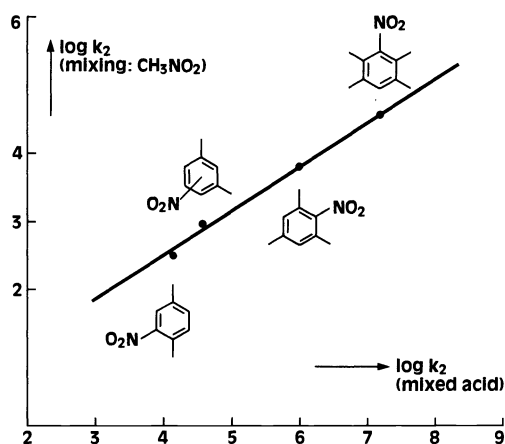
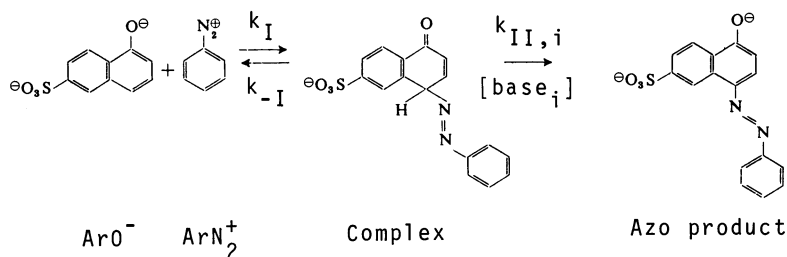


Fig. 6. Comparison between the k_2 -values determined by nitration experiments in 75,5% sulfuric acid (Ref. 22) and the k_2 -values evaluated from the selectivity curves in Fig. 5.

With the help of the MIRE model the other surprising experimental facts mentioned at the beginning of this lecture can also be explained. Like the nitration of the aromatic compounds, the coupling reaction of phenyldiazonium ion with 1-naphthol-6-sulfonic acid is also a competitive consecutive reaction system. The characteristics of this coupling reaction are discussed in full detail elsewhere (Ref. 12). Here, we shall recall only those features of the reaction which are most important for understanding the influence of the mixing process on the final product distribution:

In azo coupling reactions with naphthols the reacting species are the naphtholate ion and the diazonium ion. The bond-making and bond-breaking events are commonly agreed to follow a two step mechanism (Ref. 23). In the following scheme this mechanism is formulated for the p-coupling in the reaction system under discussion. Similar mechanistic considerations apply also for the secondary coupling. In this case ArO^- is understood to be the naphtholate anion of R.



Scheme. Two step mechanism of the azo coupling reaction.

If the steady-state approximation

$$\left| \frac{d[\text{Complex}]}{dt} \right| \ll k_I [\text{ArO}^-] [\text{ArN}_2^+] \quad (10)$$

applies, the coupling rate can be expressed as follows.

$$r = \frac{k_I \sum_i k_{II,i} [\text{base}_i]}{k_{-I} + \sum_i k_{II,i} [\text{base}_i]} [\text{ArO}^-] [\text{ArN}_2^+] \quad (11)$$

Here r : molar rate of production of the azo product
in $\text{mol dm}^{-3} \text{ s}^{-1}$
 $[\text{ArO}^-]$: concentration of the naphtholate anion
in mol dm^{-3}
 $[\text{ArN}_2^+]$: concentration of the phenyldiazonium ion
in mol dm^{-3}
 $[\text{base}_i]$: concentration of the base i in mol dm^{-3}
 $k_I, k_{-I}, k_{II,i}$: intrinsic n -order rate constants
in $\text{mol}^{1-n} \text{ dm}^{3n-3} \text{ s}^{-1}$

Assuming that the acid-base equilibria of the reacting species are established at a much faster rate than the substitution reaction occurs, we can rewrite equation (11) in terms of the total concentrations of the reactants present. For this purpose the following expressions have to be considered.

$$[\text{ArOH}]_{\text{tot}} = [\text{ArOH}] + [\text{ArO}^-] \quad (12)$$

$$K_{\text{OH}} = [\text{ArO}^-] [\text{H}^+] / [\text{ArOH}] \quad (13)$$

$$[\text{ArN}_2^+]_{\text{tot}} = [\text{ArN}_2^+] + [\text{ArN}_2\text{OH}] + [\text{ArN}_2\text{O}^-] \quad (14)$$

$$K_1 = [\text{ArN}_2\text{OH}] [\text{H}^+] / [\text{ArN}_2^+] \quad (15)$$

$$K_2 = [\text{ArN}_2\text{O}^-] [\text{H}^+] / [\text{ArN}_2\text{OH}] \quad (16)$$

As $K_1 < K_2$, the concentration of the phenyldiazohydroxide can be neglected ($[\text{ArN}_2\text{OH}] \approx 0$). One obtains then the following equations.

$$r = k [\text{ArOH}]_{\text{tot}} [\text{ArN}_2^+]_{\text{tot}} \quad (17a)$$

$$k = \frac{k_I \sum_i k_{II,i} [\text{base}_i]}{k_{-I} + \sum_i k_{II,i} [\text{base}_i]} \left(\frac{K_{\text{OH}}}{K_{\text{OH}} + [\text{H}^+]} \right) \left(\frac{[\text{H}^+]^2}{K_1 K_2 + [\text{H}^+]^2} \right) \quad (17b)$$

Here k : experimentally measured second-order rate constant for a given constant pH and given, constant concentrations of the bases i in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

In a similar way, such rate constants can be derived for the primary as well as for the secondary coupling step.

According to our MIRE-model the final product distribution of this mixing-disguised, consecutive azo coupling reaction is fully described, for given initial and boundary conditions, by the following four quantities α , E , $\varphi_{B,1}^2$ and $\varphi_{B,2}^2$.

$$\alpha = \frac{V_A}{V_B}; \quad E = \frac{[A]_0}{[B]_0}$$

$$\varphi_{B,1}^2 = \frac{\mathcal{R}^2 [B]_0}{D} \frac{k_{1,I} \sum_i k_{1,II,i} [\text{base}_i]}{k_{1,-I} + \sum_i k_{1,II,i} [\text{base}_i]} \left(\frac{K_{OH,A}}{K_{OH,A} + [H^+]} \right) \left(\frac{[H^+]^2}{K_1 K_2 + [H^+]^2} \right)$$

$$\varphi_{B,2}^2 = \frac{\mathcal{R}^2 [B]_0}{D} \frac{k_{2,I} \sum_i k_{2,II,i} [\text{base}_i]}{k_{2,-I} + \sum_i k_{2,II,i} [\text{base}_i]} \left(\frac{K_{OH,R}}{K_{OH,R} + [H^+]} \right) \left(\frac{[H^+]^2}{K_1 K_2 + [H^+]^2} \right)$$

Here V_A, V_B : volume of solution of the coupling component (A) and the diazonium salt (B), respectively, in dm^3
 $[A]_0 = [\text{ArOH}]_{\text{tot},0}$: initial total concentration of the coupling component in mol dm^{-3}
 $[B]_0 = [\text{ArN}_2^+]_{\text{tot},0}$: initial total concentration of the diazonium salt in mol dm^{-3}
 $k_{j,I}, k_{j,-I}, k_{j,II,i}$: intrinsic n-order rate constants of the bond-making and bond-breaking events in the primary ($j = 1$) and the secondary ($j = 2$) azo coupling reactions (cf. Scheme) in $\text{mol}^{1-n} \text{dm}^{3n-3} \text{s}^{-1}$
 $K_{OH,A}, K_{OH,R}$: acidity constants of the reactants A and R, respectively (defined in equation (13)) in mol dm^{-3}
 K_1, K_2 : acidity constants of the diazonium ion (defined in equations (15) and (16) in mol dm^{-3}
 $\mathcal{R}$: mean radius of the eddies in cm
 D : mean diffusion coefficient of the reactants in $\text{cm}^2 \text{s}^{-1}$ (For solvents of low viscosity: $10^{-5} \dots 10^{-6} \text{ cm}^2 \text{s}^{-1}$).

For given intrinsic rate constants of the primary and the secondary coupling reactions and for given acidity constants of the naphthol and the monoazo dyestuff the mixing moduli $\varphi_{B,1}^2$ and $\varphi_{B,2}^2$ can be changed by altering either the mixing conditions, and thus $\mathcal{R}$, or by varying $[B]_0$, the pH or $[\text{base}_i]$. In Fig. 7 the predicted and the experimentally obtained product distribution of the consecutive azo coupling under discussion are compared. For this comparison, the mixing rate is kept constant and the reaction conditions are chosen in such a way that the φ^2 -quantities are independent of the proton and base concentrations. Hence in Fig. 7, the change in $\varphi_{B,2}^2$ is represented solely by the change in $[B]_0$. The best agreement between the experimental results and the calculated behaviour is obtained when the value of 1 s is chosen for $\mathcal{R}^2/D$. This demonstrates the usefulness of the MIRE-model for describing the influence of the mixing rate on the product distribution of azo coupling reactions.

It is important to mention also the fact that the proton and the base concentrations determining the φ^2 -quantities are local concentrations in the reaction zone. As in each azo coupling step a proton is released the pH in the reaction zone is space and time dependent. It is also lower than the macroscopically measured pH, the pH-difference being a function of the local (microscopic) buffer capacity.

Besides the selectivity behaviour which can already be easily foreseen with the help of qualitative considerations (Fig. 3), the MIRE-model also makes predictions, not yet well understood. For example, it predicts the existence of characteristic sets of parameters for which the product distribution for

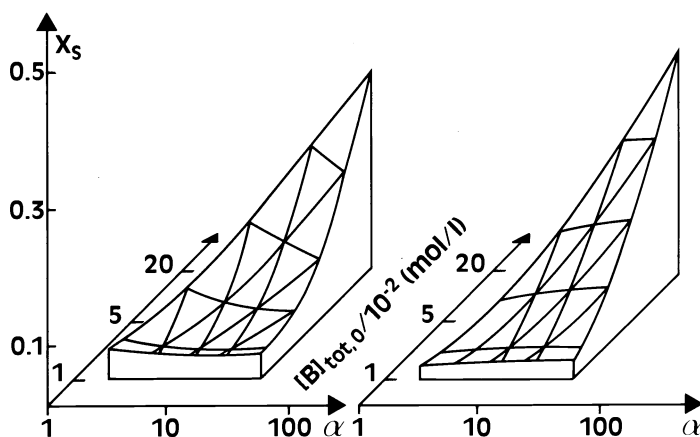


Fig. 7. Mixing-disguised azo coupling of 1-naphthol-6-sulfonic acid with diazotised aniline at pH=10.8 (22°C; $I=0.2$) (Ref. 12).
 a) Experimental results: $\alpha E=2$; $k_1/k_2=1850$. b) Calculated behaviour $\alpha E=2$; $\varphi_{B,1}^2/\varphi_{B,2}^2 \geq 100$; $\mathcal{R}^2/D=1$; (I is the ionic strength).

azo coupling reactions does not depend on the initial pH-value. These sets of parameters define the so-called isoselectivity points (Ref. 24). A more comprehensive mathematical analysis of the general behaviour of mixing-reaction systems and further experimental work to establish the existence of these isoselectivity points are in progress.

Finally, it remains to give an explanation for the third of the experimental observations mentioned at the beginning of the lecture. If one investigates the isomer ratio of the dibromo products in the bromination of resorcinol one finds that the relative proportion of the 2,4-isomer increases with increasing intensity of stirring. This result cannot be a consequence of positional selectivity determining the isomer distribution, for the positional selectivity does not depend on diffusion effects. In fact, it can be shown (Ref. 25) that the 2,4-dibromo isomer is formed via the resorcinolate or monobromoresorcinolate, whereas the 4,6-dibromo isomer is formed from resorcinol derivatives. Thus, the isomer ratio is a function of substrate selectivity and can therefore be influenced by diffusion effects. In principle, it is also possible to calculate with the help of the MIRE-model the product distribution of such competitive parallel reaction systems which are subject to mixing-disguise (Ref. 19), but only if the intrinsic kinetics of the reactions involved are known. For the bromination of resorcinol this is not yet the case. Therefore, we can only give a qualitative explanation for the experimental observations. The substrate ratio resorcinol/resorcinolate, and hence also the isomer ratio of the dibromo products, depends on the pH of the reaction solution. Since protons are liberated during the bromination, the pH in the reaction zone decreases with time. The consequence is that in the reaction zone the 4,6-dibromo isomer is formed in preference as the reaction continues. With intensive stirring the pH gradient is more rapidly destroyed, shifting the isomer ratio in favor of 2,4-dibromoresorcinol.

CONCLUDING REMARKS

This lecture has been an excursion into a hitherto neglected area of chemical kinetics. Its intention has been to provide with the help of a simple mixing-reaction model an insight into the behavior of mixing-disguised reaction systems. Although the model is simple, it is capable of refinement, if that should prove necessary. For example, the simplifying assumption of a constant eddy size could be given up, and instead the size of the liquid element as a function of time could be built into the model. This and similar refinements do not at present promise to reveal any essentially new aspects. In future work, there are still many interesting problems to be solved such as, for

example, the question as to what influence mixing might have on the product distribution in competitive autocatalytic or other more complex reaction systems.

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