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The Mixing-Sensitive Product Distribution of Chemical Reactions

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Abstract. The rate of mixing might exert a decisive influence on the product distribution in competitive chemical reactions. This review gives an account of existing mixing-sensitive single-phase liquid-liquid chemical reactions where all reactants and products are soluble, and which have the potential to be employed as an exploratory 'microprobe' to investigate the local flow characteristics and the mixing process at the molecular scale. In addition, the appropriate literature references are given to the existing theoretical *ad hoc* mixing-reaction models and to the recent progress in simulating the coupling between mixing and chemical reaction by numerical calculations.

1. Introduction

Many chemical reactions are so fast relative to mixing that significant conversion takes place before homogenization down to the molecular scale is reached. In such cases, the bond-breaking and bond-forming events mainly occur in regions where concentration gradients are still present. Consequently, the mixing process can have a pronounced effect on the kinetics and the product distribution in competitive reaction systems.

2. Coupling between Mixing and Chemical Reactions

A number of models have been proposed which claim to describe and to simulate the influence of mixing processes on the rates of chemical transformations. They have been discussed in several review papers [1–6]. It seems to be widely accepted that the mixing of miscible fluids consists of three stages. It is useful to distinguish them, even though, in practical reaction systems, they may overlap:

- Distribution of one fluid through the other. This process is brought about by ordinary eddy diffusion and causes uni-

formity of the time-average composition in different parts of a cross-section of the fluid stream without decreasing local variations.

- Subdivision of large regions of a given composition into smaller regions by the formation of vortices and by laminar and turbulent stretching. This stage increases the area of contact between regions of different composition, thus facilitating the subsequent mixing stage.
- Molecular diffusion which smooths out concentration gradients. The reactants interdiffuse, whereby molecules of each type migrate into an environment containing molecules of the other type. This creates a reaction zone in which all the reactants co-exist until the bond-breaking and bond-forming events of the chemical transformations take place. The size of the reaction zone depends on the intrinsic chemical reaction rates. This final mixing stage (micromixing) has proved to be essen-

tial for the product distribution (selectivity) of mixing-sensitive chemical reactions.

A more detailed discussion of these mixing processes has already been given in [7]. In spite of extensive theoretical work which has been published on the subject, the mixing processes are far from being clearly understood. Thus, the existing *ad hoc* mixing-reaction models can only give an order-of-magnitude estimate of the influence which the rate of mixing exerts on the distribution of the chemical reaction products.

A better understanding of the coupling between mixing and chemical reaction is needed for two reasons:

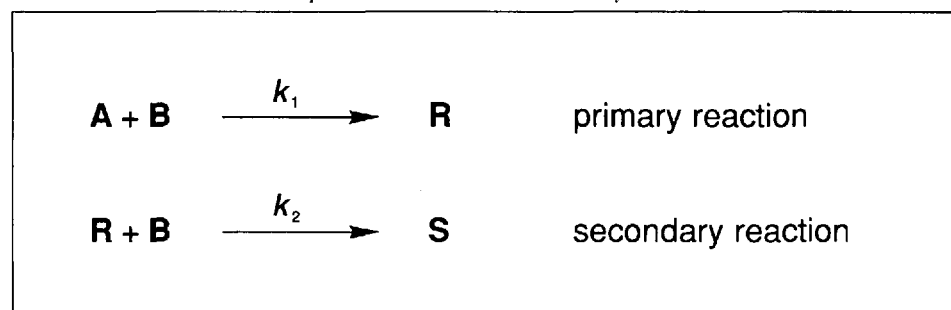
- It would enable one to evaluate the mechanism of chemical reactions even from measured chemical selectivities, which are subject to mixing-disguise.
- It would allow one to control and to optimize the product distribution of mixing-sensitive chemical processes by choosing the appropriate reactor geometry and mixing conditions.

3. Mixing-Sensitive Chemical Reactions

For the investigation of mixing effects and their influence on product distribution in competitive chemical reactions, it is inevitable to compare the numerical calculations and the theoretical predictions with experimental data. Such a comparison will then allow to select from the many *ad hoc* mixing models the one most compatible with physical reality. On the other hand, a well characterized reaction system can also be employed as an exploratory 'microprobe' which would give decisive and new information about the local flow characteristics and the mixing process at the molecular scale. However, the relatively few experimental investigations do not yet permit a thorough and comprehensive evaluation of this kind. Moreover, it is precisely for mixing-sensitive rapid reactions that the intrinsic kinetics essential for the comparison is so often unknown.

This paper gives an account of existing

Scheme 1. Unidirectional Competitive Consecutive Reaction System



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as well as some new mixing-sensitive single phase liquid-liquid chemical reactions where all reactants and products are soluble and which have the potential to be employed as a tool to investigate the mechanism of mixing on the molecular scale. It is not intended, however, to be exhaustive.

Most of the following chemical reaction systems whose product distribution is mixing-sensitive have not been designed to study the coupling between mixing and chemical reaction, but have rather been found accidentally. For the reason of clarity, these reaction systems are often classified according to the kinetic interrelation of their competing chemical events.

3.1. Competitive Consecutive Reaction System

Up to now, in all experimentally investigated mixing-sensitive reaction systems belonging to this class, the competing reactions are unidirectional as shown in *Scheme 1*.

Here, four different molecules **A**, **B**, **R**, and **S** are involved. The second reaction consumes the primary product **R** of the first one, and both are consuming **B** concurrently.

3.1.1. Aromatic Nitrations

Mixing-sensitive product distributions have long been suspected in aromatic nitrations. In many studies the remarkable observation has been reported that the equimolar nitration of durene (1,2,4,5-tetramethylbenzene, see *Scheme 2*) resulted in mainly dinitrodurene and unchanged durene, hardly any mononitrodurene was found [8–11]. Similar observations have been made with other substrates [11–14]. These experimental results are in apparent contradiction to the general knowledge of the mechanism of electrophilic aromatic substitution, according to which the second nitration should be slower than the first by a factor of $> 10^4$, i.e. $k_1/k_2 > 10^4$, because of the deactivating effect of the first NO_2 group. Some authors attempted to explain the apparently faster second nitration by reaction mechanistic considerations [15] [16]. Many other authors, on the other hand, suggested that mixing effects be the possible cause [9][10][17–19]. However, it was not before the early seventies, when these speculations were substantiated by comparing the experimental with the predicted mixing-disguised product distributions [1][2][11–13][20]

[21]. The latter were calculated for a batch reactor [20] and a continuous stirred tank reactor [22] using a simplified mixing-reaction model. This comparison is, strictly speaking, possible only because the intrinsic kinetics of the chemical reaction is known: the nitration by nitronium salts is of first order with respect to both the aromatic substrate and the nitronium ion [14].

Unfortunately, the fast nitrations are applicable to the investigation into the coupling of mixing with chemical processes only if the absolute exclusion of moisture can be achieved as, e.g., in small reaction vessels [11–13][20]. In reaction vessels of industrial size where traces of moisture can hardly be completely excluded, the nitronium ion reacts readily with water to yield nitric acid. Therefore, the effective nitronium ion concentration and thus the nitration rate decrease. As a consequence, the mixing process loses its influence on the product distribution.

3.1.2. Azo Coupling Reactions

Azo coupling is another reaction that is often disguised by mixing. 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 bis-azo product. We have demonstrated earlier on [1][2][21] [23] that the final relative product ratio of the monoazo to the bis-azo compound varies with the stirring rate, and that at high stirring rates the undesired by-product, namely the bis-azo compound, vanishes (*Fig. 1*). Soon after we published our results, various research groups began to evaluate the possibility of using fast azo coupling reactions to test the mixedness in large scale reaction vessels and to evaluate the mixing efficiencies of industrial stirring devices [24][25]. For such test reactions to be widely applicable some of the following requirements are *sine qua non*:

- the product distribution must be markedly influenced by the rate of mixing;
- for practical reasons, the competitive reactions must be chosen so that they can easily be performed in aqueous solutions;
- the intrinsic kinetics of the bond-making and bond-breaking chemical events must be known.

With azo coupling reactions the prerequisites *i* and *ii* can easily be fulfilled. Referring to the condition *iii*, in most of the aforementioned studies it was assumed that the competitive reaction system complies with the simplified *Scheme 1* and that the primary as well as the secondary azo coupling reaction follows an intrinsic kinetic of second-order, i.e. first order with

Scheme 2. Schematic Representation of the Competitive Consecutive Nitration of Durene by $\text{NO}_2^+ \text{PF}_6^-$ in Nitromethane (20°) [11]

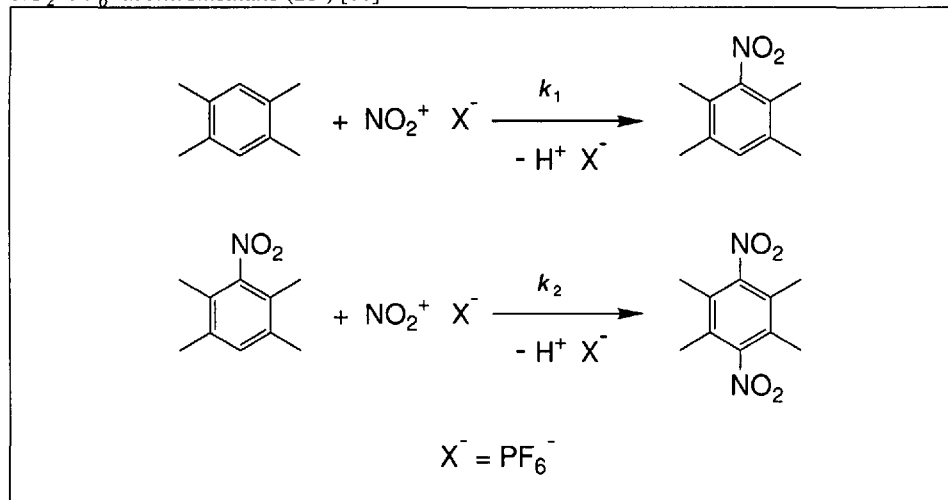
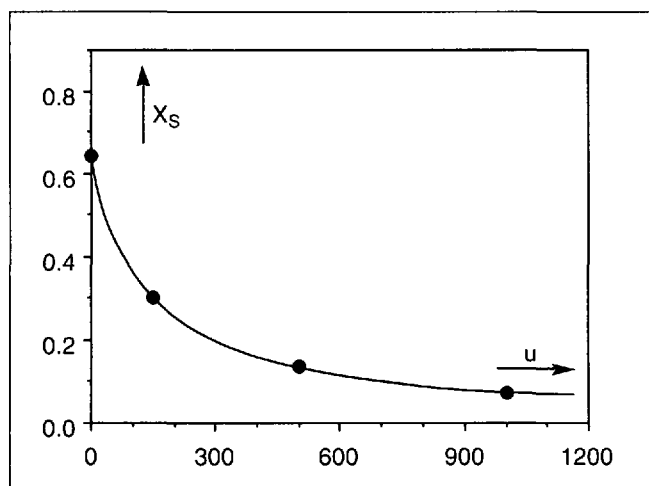


Fig. 1. Influence of the stirring rate on the product distribution in the azo coupling of 1-hydroxynaphthalene-6-sulfonate with phenyldiazonium ion in H_2O [23]. X_S : relative yield of the bis-azo product **S** at 100% conversion; u : rate of stirring [rev. min^{-1}].

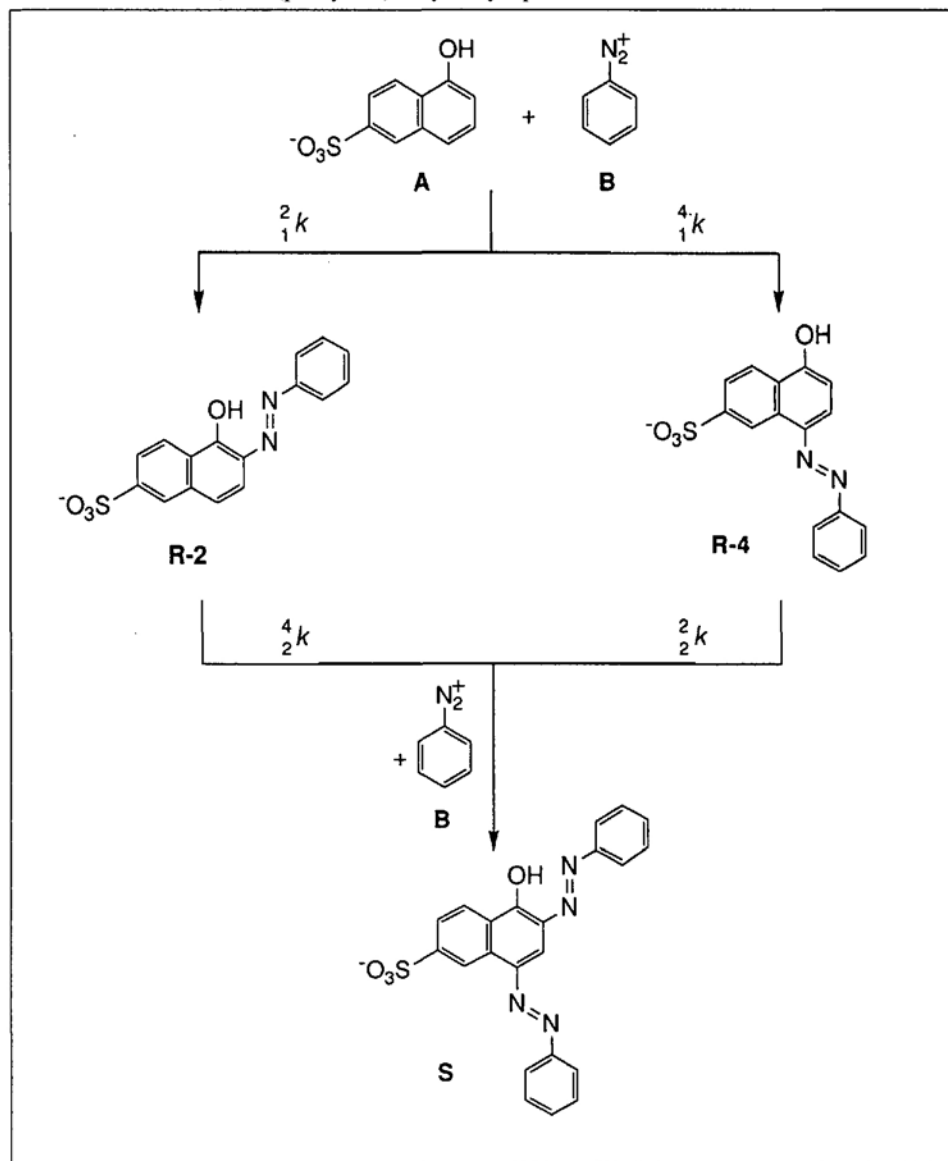


respect to the reactants **A**, **B**, and **R**. However, as we have pointed out earlier [1][2][23], such a simplified assumption can only be justified for specific reaction conditions. It seems that this restriction has mostly been ignored in the past, and it is only recently that some of the limitations were restated [26]. Evidently, if one intends to use a competitive azo coupling reaction as a 'microprobe' to evaluate the mechanism of the mixing process and its influence on the product distribution, the exact intrinsic kinetics of all reaction steps involved must first be determined. This must be done over the entire concentration range of all reactants and under all possible reaction conditions prevailing in the mixing zone.

There are various reasons why *Scheme 1* can only approximately describe the competitive consecutive azo coupling reactions of a bifunctional coupling component. This becomes evident, if all possible chemical events are considered (*Scheme 3*): First, the primary coupling of a bifunctional component generally consists of two parallel reactions, and they in turn may be mixing-sensitive. For example, in the azo coupling of 1-hydroxynaphthalene-6-sulfonate (**A**) with phenyldiazonium ion (**B**) the reaction may occur at C(2) or C(4). The bis-azo product **S** is then formed in the secondary azo coupling reaction from two monoazo products **R-2** and **R-4** that themselves differ in reactivity. Whether both of the isomers **R-2** and **R-4** are formed, and to what extent this happens depends on the individual chemical structure of the reactants **A** and **B** as well as the existing local reaction conditions. This must be carefully evaluated for every case studied. Secondly, it must be remembered that an azo coupling reaction liberates protons which even with macroscopic buffering can lead to local pH gradients in the reaction zone [1][2][23][27]. In mixing-sensitive reactions, in which these pH gradients cannot be sufficiently rapidly evened out, this leads to a shift in the preceding acid-base equilibria of the reactants in the mixing zone and, thus, influences the local reaction rates. This is quantitatively represented by the general *Rate Expression 1* for the primary ($N = A$; $j = 1$) and the secondary ($N = R$; $j = 2$) azo coupling reaction in the position n of the coupling component **N**. For the example chosen in *Scheme 3*, n is 2 or 4.

Scheme 3. Schematic Representation of a Competitive Consecutive Azo Coupling Reaction [23]

- Reactant **A**: 1-Hydroxynaphthalene-6-sulfonate.
- Reactant **B**: Phenyldiazonium ion.
- Product **R-2**: 1-Hydroxy-2-(phenylazo)naphthalene-6-sulfonate.
- Product **R-4**: 1-Hydroxy-4-(phenylazo)naphthalene-6-sulfonate.
- Product **S**: 2,4-Bis(phenylazo)-1-hydroxynaphthalene-6-sulfonate.



Here,
 $r_{j,n}$: rate of formation of the azo products **R-2** ($j = 1, n = 2, N = A$), **R-4** ($j = 1, n = 4, N = A$) and **S** ($j = 2, n = 2, N = R-4$, or $n = 4, N = R-2$), respectively.

${}^n k_j, {}^n k_{-j}, {}^n k_{II,i}$: intrinsic rate constants of the individual bond-making and bond-breaking steps in the primary ($j = 1$) and the secondary ($j = 2$) coupling reactions at the position n . The value of ${}^n k_{II,i}$ depends on the reactivity of the present base i

K_N : acidity constant of the reactant **N** ($N = A, R-2$, or **R-4**)

K_1 : acidity constant of the diazonium ion

K_2 : acidity constant of the diazohydroxide

$c_{base,i}$: concentration of the base i . In general, the bases involved are water and the components of the buffer

c_N : concentration of the coupling component **N**

c_B : concentration of the diazo component **B**

pH: $-\log c_{H^+}$

$$r_{j,n} = \frac{{}^n k_j \sum_i {}^n k_{II,i} c_{base,i}}{{}^n k_{-j} + \sum_i {}^n k_{II,i} c_{base,i}} \frac{K_N}{K_N + 10^{-pH}} \frac{10^{-2pH}}{K_1 K_2 + 10^{-2pH}} c_N c_B \quad (1)$$

The concentration terms c_N and c_B encompass all the acidic and basic species of the corresponding reactants **N** and **B**, respectively. Referring for example to the primary azo coupling reaction depicted in

Scheme 3, c_N represents the sum of the concentrations of the nonreacting 1-hydroxynaphthalene-6-sulfonate and the corresponding reactive naphtholate. Similarly, c_B encompasses the concentrations of the reactive phenyl diazonium ion and its basic nonreactive form, the phenyldiazotate. The acid-base equilibria between these species are locally established at an encounter-controlled rate [28] and, therefore, generally at a much higher rate than all other chemical events which occur. Thirdly, the primary or secondary reaction may exhibit general base catalysis. In this case, the rate of each reaction step is influenced by the local concentration gradient of the various bases i in the mixing layer (J). These and other characteristics of this azo coupling reaction are discussed in full detail in [23]. To summarize, the following requirements must be met in order that mixing-sensitive azo coupling reactions can be approximated by the simplified Scheme 1:

- In the primary reaction only one of the monoazo products is formed preferentially;
- the local buffer capacity in the mixing layer must be high enough so that the released protons can be neutralized;
- for the reaction condition used no general base catalysis should occur, *i.e.* the condition

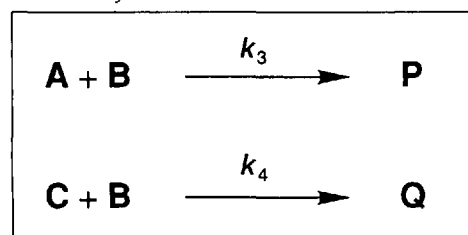
$${}_j^n k_{-1} < \sum_j {}_j^n k_{II,i} c_{\text{base},i}$$

must apply in the reaction zone for the primary as well as for the secondary azo coupling reaction.

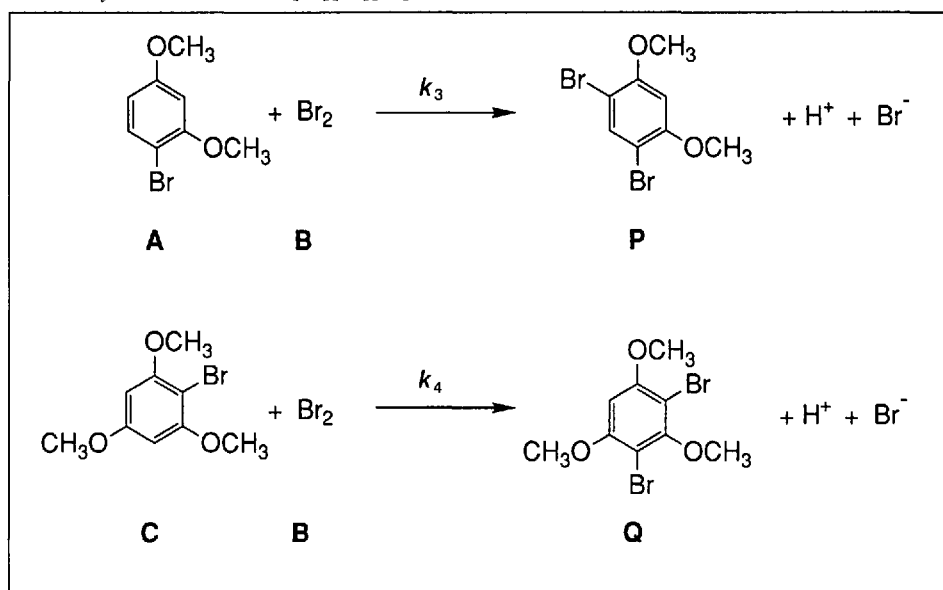
3.1.3. Other Mixing-Sensitive Reactions

The following fast competitive reaction systems have also been used to assess the influence that mixing processes may have on product distribution. However, as not in all cases has the intrinsic reaction kinetics been fully determined, the assessments of mixing effects were, therefore, only qualitative. Mixing dependent product distributions have been observed with the iodination of 1-tyrosine [29][30] and

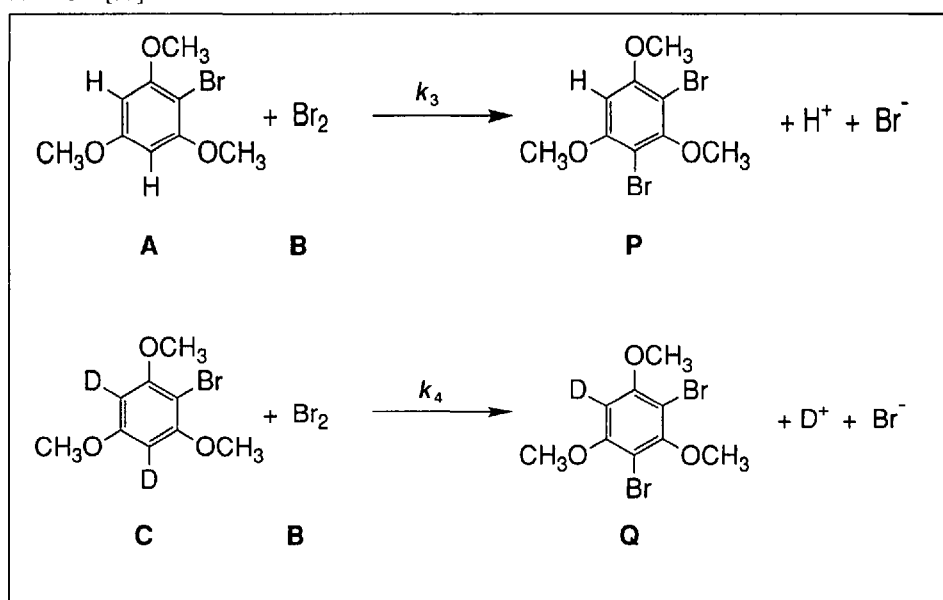
Scheme 4. Unidirectional Competitive Parallel Reaction System



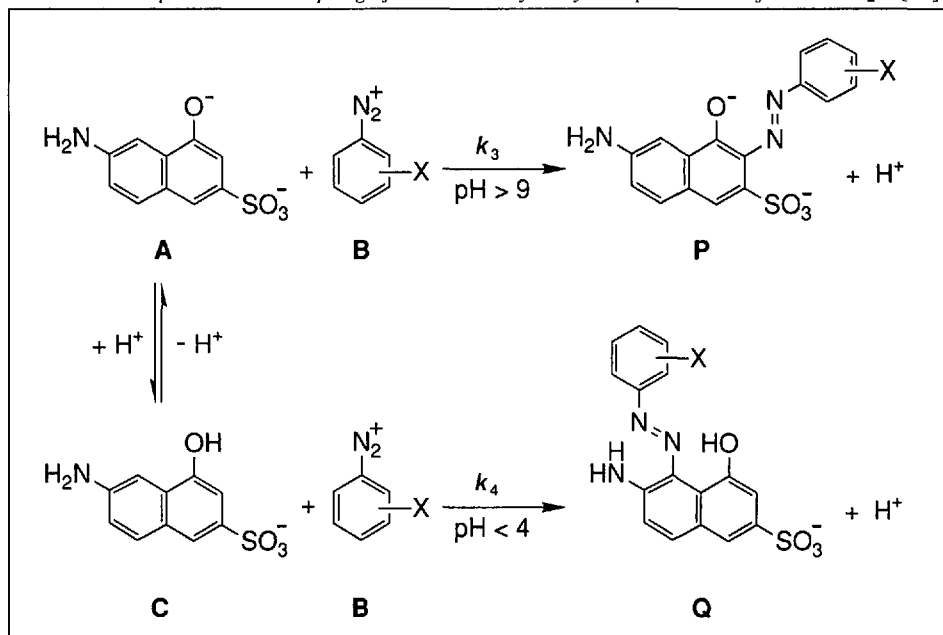
Scheme 5. Competitive Bromination of 4-Bromo-1,3-dimethoxybenzene and 2-Bromo-1,3,5-trimethoxybenzene in MeOH [35][43][45]



Scheme 6. Competitive Bromination of 2-Bromo-1,3,5-trimethoxybenzene and its Deuterated Isomer in MeOH [35]



Scheme 7. Competitive Azo Coupling of 6-Amino-4-hydroxy-2-naphthalenesulfonate in H2O [36]



p-cresol [31], with the alkaline catalyzed hydrolysis of glycol diacetate [31][32], and with competitive radical-chain reactions [47]. Further kinetic studies need to be carried out before these reactions can be adopted as test systems. Some fast polymerizations [33] have also shown the sensitivity to mixing, but in general the reaction mechanisms are very complex, and they are by no means fully understood.

3.2. Competitive Parallel Reaction System

Here, the substrates **A** and **C** compete in two parallel reactions for the same reactant **B**. In case that both reactions are unidirectional (Scheme 4), and that each of them is first order with respect to the reactant **B** and the respective substrate **A** or **C**, the intrinsic differential selectivity is given by the expression

$$\frac{dc_P}{dc_Q} = \frac{k_3}{k_4} \frac{c_A}{c_C} \quad (2)$$

However, if the competitive reaction system is mixing-sensitive, *i.e.* at least one of the appropriate *Damköhler* numbers (= mixing moduli) is much greater than unity, the selectivity factor k_3/k_4 loses its importance in determining the observed product distribution. As model calculations show [1][2][20][35][38][45][46], such a situation occurs when the sensitivity to mixing increases.

3.2.1. Aromatic Brominations

The dependence of product distribution on stirring rate was recognized as early as 1926, with the competitive bromination of a mixture of aromatic substrates [34]. Among the many possible mixing-sensitive competitive parallel reaction systems, only two are known today to have their intrinsic kinetics carefully examined [35][43]. Both reaction systems are concurrent aromatic brominations using molecular Br_2 with MeOH as the solvent. In one case, a mixture of 4-bromo-1,3-dimethoxybenzene and 2-bromo-1,3,5-trimethoxybenzene was brominated leading to the corresponding dibromo products (Scheme 5). In the other case, the competitive bromination of 2-bromo-1,3,5-trimethoxybenzene and its isomer deuterated at C(4) and C(6) was studied (Scheme 6).

The intrinsic kinetics including all the bond-making and bond-breaking chemical reaction steps of an aromatic bromination with molecular Br_2 has proved to be very complex [35]. Here, only the most important features for the understanding of the mixing effect on the final product distribution are summarized:

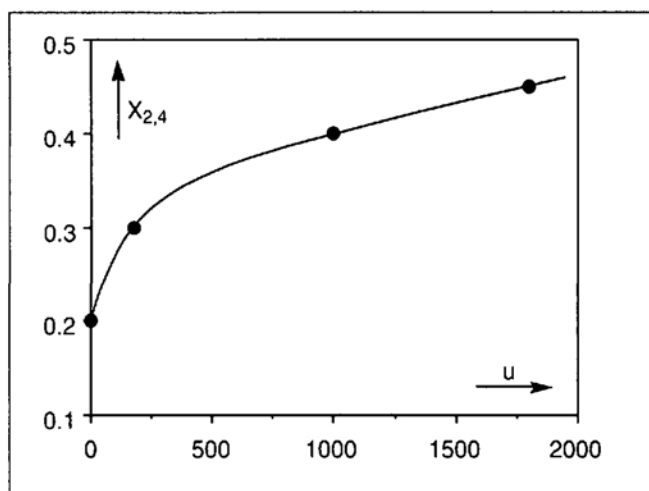


Fig. 2. Influence of the stirring rate on the isomer distribution in the competitive bromination of resorcinol with molecular Br_2 in MeOH (22°) [41]. $X_{2,4}$: relative yield of the 2,4-dibromo isomer at 100% conversion; u : rate of stirring [rev. min⁻¹].

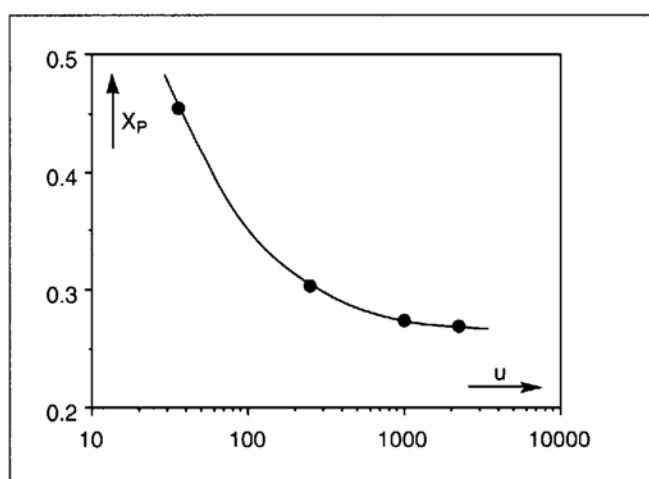


Fig. 3. Influence of the stirring rate on the isomer distribution in the competitive bromination of 1-(tert-butyl)-3-methoxybenzene in 70% MeOH (20°) [43]. X_p : relative yield of the 4-bromo isomer at 100% conversion; u : rate of stirring [rev. min⁻¹].

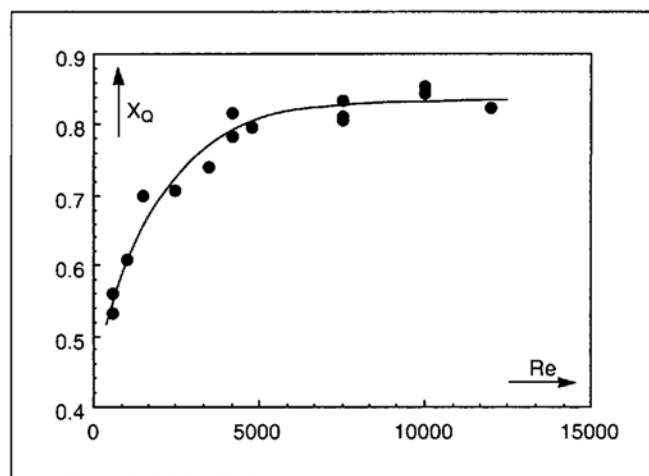


Fig. 4. Influence of the stirring rate on the isomer distribution in the azo coupling of 1-hydroxynaphthalene-3-sulfonate with 2-nitrophenyldiazonium ion in H_2O (25°) [44]. X_Q : relative yield of the 2-isomer at 100% conversion; Re : Reynolds number.

i) The brominations depicted in Schemes 5 and 6 follow the intrinsic kinetic expression (3).

Here,
 r_N : rate of bromination of substrate **N**
 $N^k_I, N^k_{-I}, N^k_{II,i}$: intrinsic rate constants of

$$r_N = \frac{N^k_I \sum_i N^k_{II,i} c_{base,i}}{N^k_{-I} c_{Br^-} + \sum_i N^k_{II,i} c_{base,i}} c_N c_{Br_2} \quad (3)$$

the individual bond-making and bond-breaking steps in the bromination of substrate N.

The value of $Nk_{II,i}$ depends on the reactivity of the base i

c_{Br^-} : concentration of bromide ion

c_N : concentration of substrate N

c_{Br_2} : concentration of Br_2

ii) These brominations liberate protons and Br^- anions, resulting in pH- and bromide concentration gradients within the reaction zone. As shown in Eqn. 3 the evolved Br^- ions can slow down the overall chemical event. According to our previous investigation [35], this happens for the bromination of the substrates A or C depicted in Scheme 5 at bromide concentrations higher than 10^{-1} or 10^{-3} mol/l, respectively. Under these conditions, a general base catalysis starts to show up.

Consequently, the bromination rate then becomes dependent on the various bases i present in the reaction zone.

iii) The rate-reducing action of the Br^- ion generated, is not only brought about by the kinetic term $Nk_{-1}c_{Br^-}$ in Eqn. 3, but also by the fact that the Br^- ion combines with Br_2 to form the Br_3^- ion in a very fast equilibrium (4). This lowers the concentration of bromine, c_{Br_2} , and thus according to Eqn. 3 also the bromination rate.



3.2.2. Azo Coupling Reactions

In the azo coupling of aminonaphthols the position at which the reaction takes place depends on the pH applied (Scheme 7). At low pH values, the coupling occurs preferentially at the aromatic ring which

bears the NH_2 group, whereas at high pH values the reaction is selectively directed into the other aromatic ring [37]. If the reaction conditions are chosen such that the mixing process is rate-determining, the isomer distribution becomes sensitive to the stirring rate [36]. In fact, if the azo coupling was performed at pH 9 to 10, not only the product P but also appreciable amounts of the product Q were formed. With increasing stirring rate, the product ratio c_P/c_Q increases [36]. This observation can be interpreted in terms of what has been discussed in 3.1.2: If the azo coupling is very much faster than the neutralization by the buffer from the bulk, of the protons released, a drop of the local pH in the reaction zone will occur. This in turn leads to a shift of the acid-base equilibrium toward the substrate C, and as a consequence more of the azo product Q is formed.

This competitive azo coupling is a suitable candidate for a model reaction to evaluate the influence of mixing processes on the product distribution of mixing-sensitive reactions. However, further extensive studies are needed to assess the intrinsic kinetics over a wide range of experimental conditions.

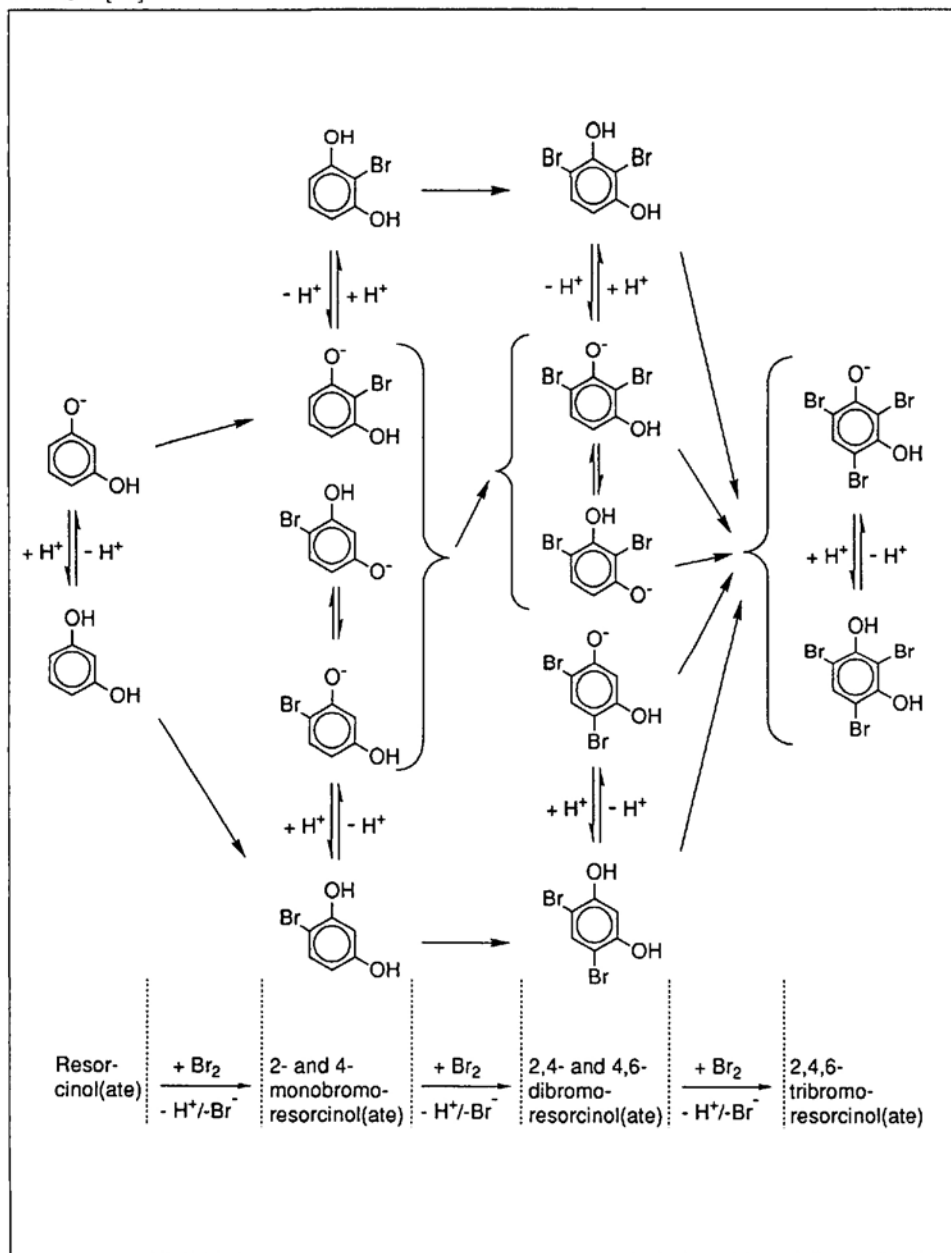
3.2.3. Other Mixing-Sensitive Reactions

A detailed study of the competitive nitration of aromatic hydrocarbon mixtures with nitronium salts has revealed that the product distribution is mixing-sensitive [39]. However, such systems are not suitable for the investigation of the mixing process, albeit the reaction mechanisms and their intrinsic kinetics are well known [14]. The reasons are given in 3.1.1 and they will not be reiterated here. Finally, the mixing-sensitive reduction of (halopentammine)cobalt(III) complexes by chromous ions is also worthy of note, although the reaction mechanisms can be complex and, like the kinetics, are not always fully known [40].

3.3. Substrate vs. Positional Selectivity

If a chemical compound has more than one reaction site, the ratio of the structural isomers in the product can be determined by the different reactivity pattern of two distinct (acid-base) equilibrium forms of the same compound. Since these equilibrium forms involve two different substrates in a competitive parallel reaction, the distribution of the isomeric products is said to be determined by a *substrate* selectivity. However, if the product distribution results exclusively from the relative reactivities of the respective positions in the same multi-site substrate, the ratio of the isomers formed is defined by the so-called *positional* (or *regio-*) selectivity.

Scheme 8. Spectrum of Products (without H^+ and Br^-) in the Competitive Bromination of Resorcinol in MeOH [41]



3.3.1. Isomer Distribution Determined by Mixing-Sensitive Substrate Selectivity

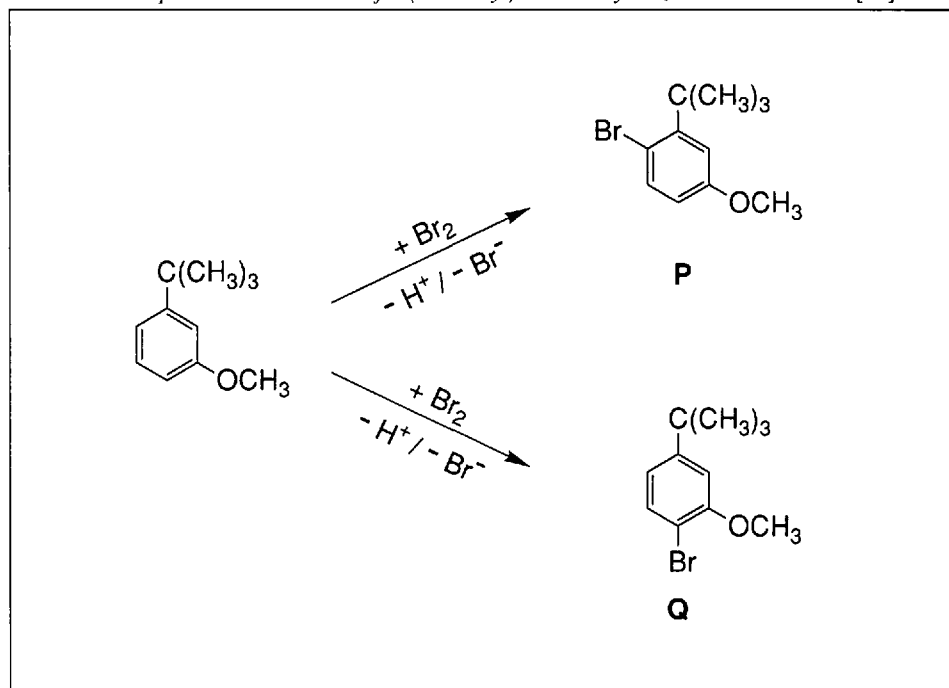
Scheme 7 shows an example of a competitive reaction system in which two isomers are formed from two different substrates identified as two distinct acid-base equilibrium forms of the same compound. A similar situation has been identified in the competitive bromination of resorcinol [1][2][41][42]. Here, however, the reaction system is extremely complex, as it consists of a superposition of consecutive and parallel chemical events occurring simultaneously: if resorcinol in MeOH is treated with an equimolar amount of molecular Br_2 , monobromo isomers are obtained in addition to dibromo isomers and 2,4,6-tribromoresorcinol [41][42]. The degree of substitution decreases when the rate of stirring is increased, *i.e.* with more effective mixing. An analysis of the ratio of the dibromo isomers in the products obtained under conditions which give mainly dibromo substitution reveals that the relative proportion of the 2,4-isomer also increases with increasing stirring rate (Fig. 2). In principle, there are two possible reasons which may explain the results. On the one hand, this finding may be a consequence of a positional selectivity (see 3.3.2), provided that the bromination at various reaction sites of resorcinol exhibits different kinetic order. So far, nobody has been able to evaluate this intrinsic bromination kinetics exactly. On the other hand, however, it has been shown [41] that the formation of 2,4-dibromo isomer proceeds *via* the resorcinolate or monobromoresorcinolate, whereas the 4,6-dibromo isomer is formed from resorcinol derivatives. This means that the ratio of the structural isomers is a function of substrate selectivity, as shown in Scheme 8.

The substrate ratio resorcinol/resorcinolate, and hence the ratio of the dibromo isomers depends on the pH of the reaction solution. Since protons are liberated during the bromination (Schemes 5, 6, and 8), the pH in the reaction zone decreases with time. As a consequence, in the reaction zone the 4,6-dibromo isomer is formed preferentially as the reaction continues. With intensive stirring, the pH gradient is more rapidly destroyed, and the isomer ratio is shifted in favor of 2,4-dibromoresorcinol.

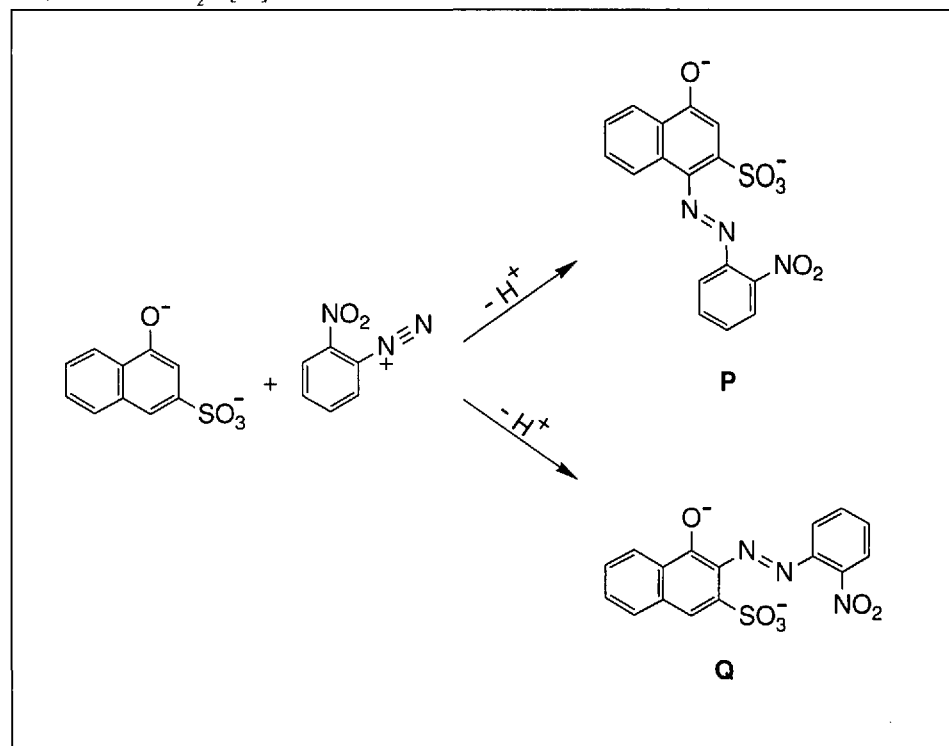
3.3.2. Isomer Distribution Determined by Mixing-Sensitive Positional Selectivity

It is important to draw attention to the fact that a product distribution, which is solely a consequence of positional (*regio-*) selectivity, can be altered by mixing effects only if the competing reactions have a difference in kinetic order with

Scheme 9. Competitive Bromination of 1-(*tert*-Butyl)-3-methoxybenzene in 70% MeOH [43]



Scheme 10. Competitive Azo Coupling of 1-Hydroxynaphthalene-3-sulfonate with 2-Nitrophenyldiazonium Ion in H_2O [44]



respect to at least one of the reagents. These aspects are of great importance in our recent [43][44] and continuing efforts to design a competitive mixing-sensitive reaction system suitable for the evaluation of mixing process mechanism. In electrophilic aromatic substitutions, the most mixing-sensitive positional selectivities can be obtained, if one of the competing reactions is sterically hindered and hence exhibits a general base catalysis. This has been clearly demonstrated by the bromination of 1-(*tert*-butyl)-3-methoxybenzene with molecular Br_2 (Scheme 9 and Fig. 3)

[43] and for the azo coupling of 1-hydroxynaphthalene-3-sulfonate with 2-nitrophenyldiazonium ion (Scheme 10 and Fig. 4) [44]. In these detailed studies, it has been carefully elucidated that both reactions, bromination at the position *ortho* to the *t*-Bu group, and the *para* azo coupling, are catalyzed by the bases present in the respective reaction zones. An increase in stirring rate decreases the concentration of the added bases within the reaction zone and, as a consequence, the rate of formation of the corresponding products P.

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