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Mechanism of Azo Coupling Reactions: Part XXXVI.[1) The Relationship between the Structure and the Catalytic Activity of Anionic Phase-Transfer Catalysts in Azo Coupling Reactions

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A series of 15 sodium arenesulfonates containing alkyl, hydroxyl or methoxyl groups was investigated for the phase-transfer catalysis of the azo coupling reaction of the 4-methoxybenzenediazonium ion (**1**) with 1,3,5-trimethoxybenzene (**2**) in a dichloromethane/water two-phase system, in which the yields, initial reaction rates and influence of the decomposition of the diazonium ion **1** were measured. The influence of counter anions on the partition coefficient (α) for the diazonium ion **1** in a dichloromethane/water system, and the effects of the solvent polarity and structure of counter anions on the reaction rates of the azo coupling of the diazonium ion **1** with *N,N*-dimethylaniline (**4**) and 1,3,5-trimethoxybenzene (**2**) in organic solvents and in dichloromethane/water system, were investigated. The symmetrical structure of the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) anion was proved to be an essential factor regarding the remarkably high α for the diazonium ion **1** ion-paired with TFPB. The looseness and tightness of ion pairs of highly desolvated diazonium ion **1** in a nonpolar organic media is one of the most significant factors concerning the reactivity of the diazonium ion **1** in a rate-limiting azo coupling with **4**. In a reaction of the diazonium ion **1** with **2** in a dichloromethane/water system, however, the amount of saturated water and/or additives in the dichloromethane phase, which serves as a base for the rate-limiting deprotonation, becomes the most influential factor for an effective azo coupling reaction under phase-transfer catalysis conditions.

Phase-transfer catalysis (PTC) allows reactions to be carried out with ionic reagents in aprotic solvents, or with reagents that are lipophilic and poorly soluble in water. The rates and yields under PTC conditions may be higher than those in conventional one-phase system. The general concept of PTC applies to the transfer of any species from one phase to another, if a suitable catalyst can be provided with appropriate phase compositions and reaction conditions. A large majority of the PTC investigations were carried out involving reactions in which an anionic reagent was extracted from an aqueous into an aprotic phase with cationic species, such as quaternary ammonium or phosphonium ions or crown ethers as catalysts. The influence of the structure of these catalysts on the efficacy of cation-catalyzed PTC has been widely investigated in a variety of nucleophilic and base-mediated reactions.[2) On the other hand, relatively little is known concerning anion-catalyzed PTC, in which lipophilic anionic species catalyze the transfer of cationic reagents from the aqueous or solid phase to the organic phase, thus and promoting electophilic reactions (Fig. 1). This is mainly due to a lack of efficient or available anionic catalysts for this purpose.

A few examples of azo coupling reactions of arenediazonium ions in a PTC system have been reported. Bredereck and Karaca[3) found that PTC, upon the addition of 50 mol% of Nekal BX (a mixture of sodium mono- and di-*t*-butylnaphthalenesulfonates), increased the yield of the azo coupling on 1-naphthol by 40%. Ellwood, Griffiths, and Gregory[4) successfully used sodium dodecylbenzenesulfonate (NaDBS) for PTC in the reaction of 4-nitrobenzenediazonium ions with *N*-ethylcarbazole and diphenylamine.

Experience in PTC with cationic catalysts has shown that, in general, those compounds that are particularly suitable are of symmetrical structure and are lipophilic; also, the active cationic charge is either cen-

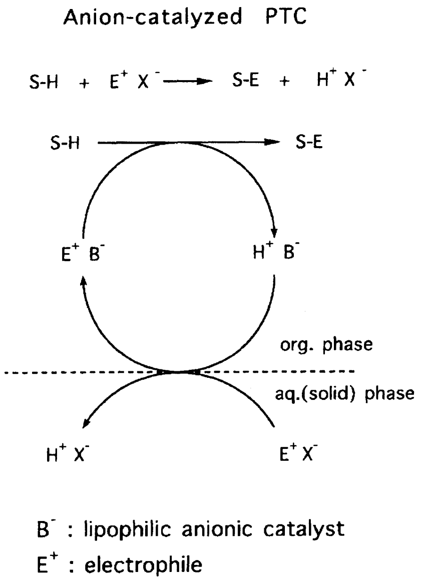

Fig. 1. Catalytic cycle in anion-catalyzed phase-transfer catalysis.

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trally located, or is sterically shielded by substituents. For anionic catalysis, sodium tetraphenylborate fulfills these conditions. This compound is not, however, stable under acidic conditions.[5] Nevertheless, Sonoda, Kobayashi, and co-workers[6] have found that derivatives of this compound, namely sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) and sodium tetrakis[3,5-bis(1-methoxy-1-trifluoromethyl-2,2,2-trifluoroethyl)phenyl]borate (HFPB), are sufficiently stable to be used as PTC catalysts. They applied these compounds to various reactions involving cationic reagents,[7] including azo coupling. Both of these tetraphenylborates with fluorinated methyl groups strongly catalyzed azo coupling reactions with the respective diazotization in situ.

Tamagaki et al.[8] investigated the liquid–solid PTC of azo coupling reactions using silica gel. The diazonium ion is activated by sorption to silica gel. The yields were found to be better than in liquid–liquid PTC with NaDBS.

Crown ethers solubilize diazonium ions in aprotic solvents, as shown in the pioneering work of Cram et al.[9] Juri and Bartsch[10] found that the 18-crown-6 complex of the 4-*t*-butylbenzenediazonium ion shows a reactivity in the azo coupling with *N*,*N*-dimethylaniline in 1,2-dichloroethane that is 8.3-times lower than the uncomplexed tetrafluoroborate in that solvent. Hashida et al.[11] found, however, that the azo coupling reaction of the 4-diethylaminobenzenediazonium ion with the potassium salt of 5,5-dimethylcyclohexane-1,3-dione in acetonitrile is catalyzed by 18-crown-6 by a factor of 2.5. Butler and co-workers[12] also reported the successful use of crown ethers with 4-nitro-, but not with 4-methoxybenzenediazonium, ions. It is therefore doubtful whether crown ethers are good candidates for the PTC of azo coupling reactions. Effective catalysts are the anions of picric acid and 2,4-dinitro-1-naphthol, as was found by Hashida et al.[11]

All of these investigations were made with combinations of either strongly electrophilic diazonium ions and good to weak coupling components, or relatively weak diazonium ions with highly reactive coupling components. We think that it would be more interesting to investigate the application of PTC to such azo coupling reactions that do not proceed in water at all, or with extremely low rates and at low yields.

We therefore report in this paper on an investigation of the azo coupling reaction of the 4-methoxybenzenediazonium ion (**1**) with 1,3,5-trimethoxybenzene (**2**), i.e. a reaction that gives after 12 d a yield of only 0.26% of the azo product, 2,4,4′,6-tetramethoxyazobenzene (**3**), without using a catalyst. As catalysts we used a series of sodium benzene- and naphthalenesulfonates with various aliphatic substituents, and, in part, with a hydroxyl or methoxyl group. These compounds are relatively easy to obtain and may therefore be interesting for large-scale industrial azo coupling reactions.

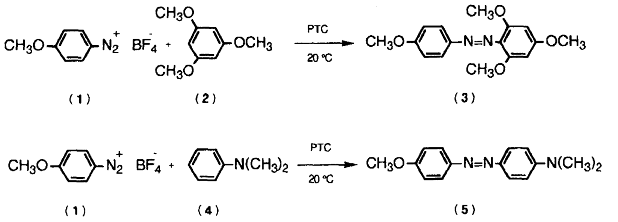


Chart 1.

Furthermore, in order to elucidate the mechanism of the azo coupling reactions under PTC conditions, we report here on the azo coupling reactions of the diazonium ion **1** with *N*,*N*-dimethylaniline (**4**) to give 4-dimethylamino-4′-methoxyazobenzene (**5**) and with 1,3,5-trimethoxybenzene (**2**) to give **3** in the presence of several organic anions as a PTC catalyst in organic solvents and in a dichloromethane/water system (Chart 1). We studied the following points:

1) The influence of counter anions on the partition coefficient for the diazonium ion **1** in a dichloromethane/water system. It is well known that the primary effect of PTC on the yield is to increase the reagent in the organic phase. This is also the case for the azo coupling reactions.

2) The effects of the solvent polarity and the structure of the anionic catalysts on the rate and yield of the azo coupling reactions. The reactivity of diazonium ions in organic solvents is closely related to the specific solvation of the diazonium ions as well as the interaction with counter anions.

Result and Discussion

The Azo Coupling Reactions of the Diazonium Ion 1 with 1,3,5-Trimethoxybenzene (2) in the Presence of Sodium Arenesulfonates as PTC Catalysts in Dichloromethane/Water System. 4-Methoxybenzenediazonium tetrafluoroborate (**1**) is known to be a relatively stable compound in both the solid state and in an aqueous solution.[13] We determined its solubility in dichloromethane to be 478 mg dm^{-3} (2.15×10^{-3} mol dm^{-3} at 20 °C). 1,3,5-Trimethoxybenzene (**2**) is easily soluble in dichloromethane; we also determined the solubility in water: 354 mg dm^{-3} (2.11×10^{-3} mol dm^{-3} at 20 °C). The yield of the reaction product, 2,4,4′,6-tetramethoxyazobenzene (**3**), was determined by capillary GC in a series of samples taken from the reaction system at various time intervals between 1.00 and 18.10 d. Unless mentioned otherwise, all of the experiments were run by mixing 2.25 mmol of the diazonium salt and 0.1125 mmol of the catalyst (5 mol%) in 50 cm^3 of an aqueous phosphate buffer (pH=7.0) with a solution of 2.25 mmol of 1,3,5-trimethoxybenzene (**2**) and ca. 250 mg of dibutyl phthalate as the internal standard (for GC analysis) in 50 cm^3 of dichloromethane. The reaction mixture was kept and agitated in a black Erlenmeyer flask, which was maintained at 20.0±0.1 °C.

Some representative results are given in Figs. 2 and 3. The results with no catalyst, and those with two weak catalysts, are shown in Fig. 2: After 12 d, yields of only 0.26, 0.33, and 0.99% were obtained. The results with catalysts containing a hydroxyl or a methoxyl group, respectively, are shown in Fig. 3. Here, yields of up to 35% are obtainable after 15 d. With two of the catalysts, even better yields may be obtained after longer reaction times. Measurements of the type (as shown in Figs. 2 and 3) may be used to calculate the first- and second-order rate constants. They are not, however, accurate since heterolytic and homolytic decompositions are competitive reactions. Such reaction systems can be handled reliably only if the yield of the azo coupling product after completion, i.e. disappearance of all diazonium ions, is known.[14)] A comparison of the different types of curvature of the upper two curves of Fig. 3 shows, that this is not the case for these reactions. We therefore calculated the first-order rate constants (k_1) from the initial slopes of the curves in Figs. 2 and 3 as well as in all other experiments. The rate constants are given in Table 1. The latter also contains the result for this azo coupling reaction in a homogeneous aqueous ethanol solution (water/ethanol=1/4).

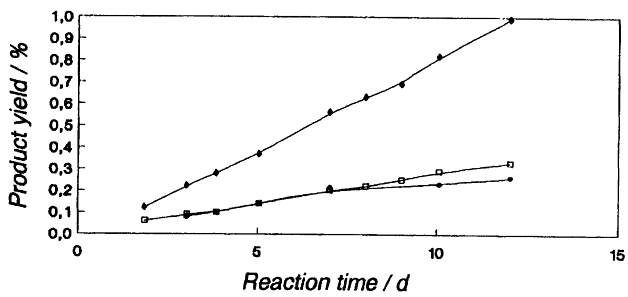


Fig. 2. Catalytic activity of alkylated benzenesulfonates on the azo coupling reaction of **1** with **2**. ● : not catalyzed, □ : benzenesulfonate, ◆ : 2,4,6-trimethylbenzenesulfonate.

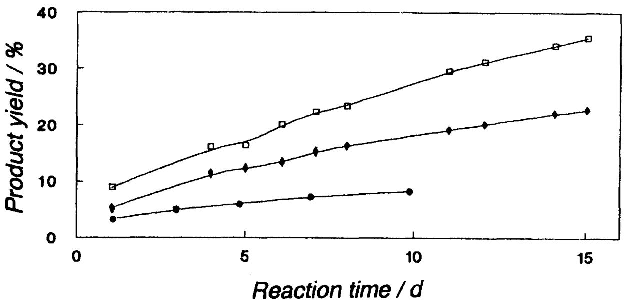
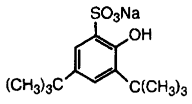
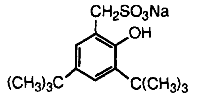


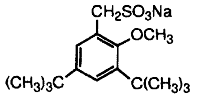
Fig. 3. Catalytic activity of 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (**6**), 3,5-di-*t*-butyl-2-hydroxyphenylmethanesulfonate (**7**), and 3,5-di-*t*-butyl-2-methoxyphenylmethanesulfonate (**8**) on the azo coupling reaction of **1** with **2**. ● : catalyst **6**, ◆ : catalyst **7**, □ : catalyst **8**.



(**6**)



(**7**)



(**8**)

A comparison of these rate constants (k_1 in Table 1) with the respective yields after 10 d shows a good linear relationship (r=0.999; n=16), although the range of the rate constants extends from 2.66×10^{-9} to 3.60×10^{-7} s^{-1}, and of the yields extend from 0.23 to 26.7% (Fig. 4).

The results given in Table 1 and Figs. 2 and 3 demonstrate that benzenesulfonate has practically no catalytic effect on this azo coupling reaction. The two isomeric naphthalenesulfonates show a small effect. The separation of the slightly electron-withdrawing sulfonic group[15)] from the naphthalene ring by a methylene group (1- and 2-naphthylmethanesulfonate, last two entries of Table 1) has no, or only a neglegibly small, effect relative to 1- and 2-naphthalenesulfonate, although it has been shown by Koller and Zollinger[16)] that the capability to form a charge-transfer (CT) complex of the 2-nitrobenzenediazonium ion with 1-naphthylmethanesulfonate *in water* is 3.6-times higher than that with 1-naphthalenesulfonate.

Substitution of benzene- and 1-naphthalenesulfonate with alkyl groups increases the catalytic effect significantly. The best catalyst is the derivative of benzenesulfonate with a hydroxyl group in the 2-position and *t*-butyl groups in the 3- and 5-position (**6**). Separation of the sulfonic group in this compound by a methylene group (**7**) strongly decreases the catalytic effect relative to **6**. Methylation of the hydroxyl group of **7** improves the catalytic character again (**8**), but **8** is not as efficient as **6**.

In general, our results first demonstrate a significant increase in the rate and yield with increasing lipophilicity of the aromatic sulfonates. Based on published results involving the PTC of nucleophilic aliphatic substitution,[17)] we chose symmetrically substituted benzenesulfonates. The increasing size of the two alkyl groups in the 2- and 6-position is also probably an important factor, since it improves the charge separation in the ion pair with the diazonium ion, and decreases the Coulomb attraction, which may decrease the electrophilicity of the diazonium ion.

The combination of naphthalenesulfonate with alkyl groups is, however, obviously better than that of alkylated benzenesulfonates, although the symmetry of the two 3,7-dialkylated 1-naphthalenesulfonates is lower, and the sulfonic group is not shielded by neighboring alkyl groups. It is surprising, however, that the *t*-butyl groups do not show a larger effect than do the isopropyl groups. The better CT donor capability of naphthalene, compared to that of benzene, is, of course, already observable in the about six-times higher rates and yields of the two unsubstituted naphthalenesulfonates relative to benzenesulfonate.

The strong PTC effect of the hydroxyl group in the

Table 1. Results of Azo Coupling Reactions of 4-Methoxybenzenediazonium Tetrafluoroborate (**1**) with 1,3,5-Trimethoxybenzene (**2**) with Various Sodium Sulfonates in Dichloromethane/Water System

Catalyst (Sodium salts)	Duration experiment	Yield after 10 d	Final yield	Rate constant k_1
	d	%	%	s^{-1}
None	12.00	0.23	0.26	2.66×10^{-9}
BS[a]	12.00	0.28	0.33	3.24×10^{-9}
2,4,6-Trimethyl-BS	12.00	0.80	0.99	9.25×10^{-9}
2,4,6-Triethyl-BS	12.00	5.85	6.19	6.98×10^{-8}
Pentamethyl-BS	17.92	2.05	3.1	2.39×10^{-8}
2,4,6-Triisopropyl-BS	17.92	21.2	26.2	2.75×10^{-7}
2,4,6-Tricyclohexyl-BS	17.92	20.2	25.4	2.61×10^{-7}
3,5-Di-*t*-butyl-2-hydroxy-BS (**6**)	15.04	26.7	35.5	3.60×10^{-7}
3,5-Di-*t*-butyl-2-hydroxyphenylmethanesulfonate (**7**)	9.83	11.7	8.3	1.44×10^{-7}
3,5-Di-*t*-butyl-2-methoxyphenylmethanesulfonate (**8**)	15.04	17.2	22.7	2.19×10^{-7}
1-NS[b]	18.10	1.53	2.76	1.79×10^{-8}
2-NS	18.10	1.66	2.97	1.94×10^{-8}
3,7-Diisopropyl-1-NS	15.00	23.3	30.7	3.07×10^{-7}
3,7-Di-*t*-butyl-1-NS	15.00	22.1	29.0	2.89×10^{-7}
	32.00	—	38.7	—
1-Naphthylmethanesulfonate	18.10	1.53	2.68	1.78×10^{-8}
2-Naphthylmethanesulfonate	18.10	2.05	3.65	2.39×10^{-8}
Reaction with no catalyst in aqueous ethanol solution	12.00	—	15.0	—

a) BS: Sodium benzenesulfonate. b) NS: Sodium naphthalenesulfonate.

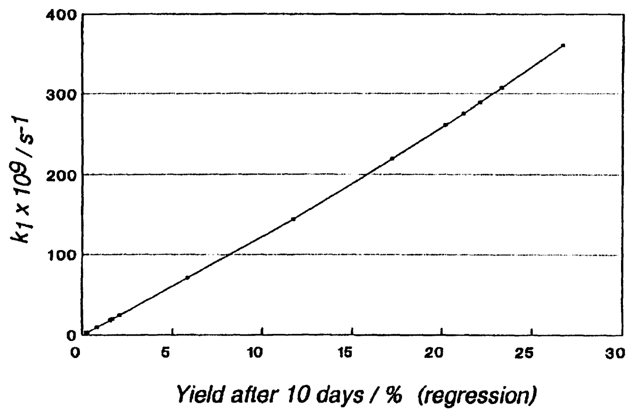


Fig. 4. Linear relationship between the yield of the azo coupling reaction after 10 d for 15 catalysts and the respective first-order rate constant (k_1).

ortho-position of the sulfonic group in compound **6** is very interesting. We chose this compound because it is known that this anion displays good cation extraction properties.[18] The intramolecular hydrogen bond in **6**, which disperses the negative charge, is probably the most important. In compound **7**, although such a hydrogen bond is also sterically possible, the more flexible position of the sulfonic group decreases the strength of that hydrogen bond. The better PTC effect of the methoxyl compound **8** relative to **7** demonstrates that the hydroxyl group in **7** decreases the lipophilicity of the anion too much.

We also determined the yield and the rate as a function of the concentration of catalyst **6** and of the acidity. The results are given in Table 2. In two additional experiments the yield was also measured with sodium 3,7-di-*t*-butylnaphthalene-1-sulfonate at two other acidities. The yields after 15 and 32 d were 22.9 and 30.9%, respectively, in deionized water and 17.6 and 24.4% in 0.1 mol dm^{-3} H_2SO_4. At pH=7.0 the yields were 29.0 and 38.7% (see Table 1).

Since the yield of the azo product is influenced by the competitive decomposition of the diazonium ion, we investigated the rate of decomposition in the dichloromethane/water system used in this work, but in the absence of 1,3,5-trimethoxybenzene (**2**) as well as in

Table 2. Influence of the Catalyst (Sodium 3,5-Di-*t*-butyl-2-hydroxybenzenesulfonate, **6**) Concentration and of Acidity on the Yield and the Rate of Formation of Azo Compound **3**

Catalyst **6**	pH	Duration of experiment	Final yield	Rate constant
mol%		d	%	$mol^{-1}\,dm^3\,s^{-1}$
5	7.0	14.00	34.0	8.28×10^{-6}
15	7.0	17.00	59.4	1.52×10^{-5}
50	7.0	14.00	69.5	2.27×10^{-5}
5	7.0	22.00	46.2	8.06×10^{-6}
5	6.0	22.00	39.5	6.49×10^{-6}
5	5.0	22.00	52.1	8.40×10^{-6}
5	H_2O[a]	22.00	29.6	6.84×10^{-6}

a) Deionized water, not buffered. The pH decreases during the reaction from 5.5 to about 2.

the absence of a catalyst. The percentages of the recovered diazonium ion found at various reaction times are given in Table 3. In addition, we determined both the percentage of the recovered diazonium ion and the azo product at various reaction times for the last four experiments listed in Table 2, i.e. at four different pH values and in the presence of catalyst **6**. The results are graphically shown in Fig. 5, which shows the sum of the percentages of the diazonium ion **1** and the azo product **3** plotted as a function of the reaction time. The difference in that sum from 100% corresponds to the amount of decomposed diazonium ion.

As expected, the rate and yield of this azo coupling reaction could be increased using higher concentrations of the catalyst, as shown for **6** in Table 2. The increase in the rate does not, however, correspond to a first-order dependence on the concentration of **6**. We will discuss this result later in the context of the determination of the partition coefficient of the diazonium ion between the aqueous and organic phases.

The influence of the acidity of the aqueous medium is complex (Table 2, last four entries): The initial rates obtained with catalyst **6** at pH 5 to 7 and in deionized water are not significantly different. The yields after 22 d are relatively high in experiments started at pH 5, 6, and 7, but lower in an experiment in deionized water. This low yield is not, however, due to a greater dominant decomposition of the diazonium ion, as shown in Fig. 5. The sum of the azo product **3** and the residual diazonium ion **1** is still 100% (within experimental error).

Table 3. Decomposition of Diazonium Ion **1** in Dichloromethane/Water System (Buffer: pH=7.00) in the Absence of 1,3,5-Trimethoxybenzene (**2**) and a Catalyst

Time / d	Recovered diazonium ion[a] / %
1.00	98.6
2.00	97.7
3.00	96.0
6.00	91.1
8.00	86.1
10.00	84.6
15.00	77.8

a) Initial concentration of $1=5.63\times10^{-2}$ mol dm^{-3}.

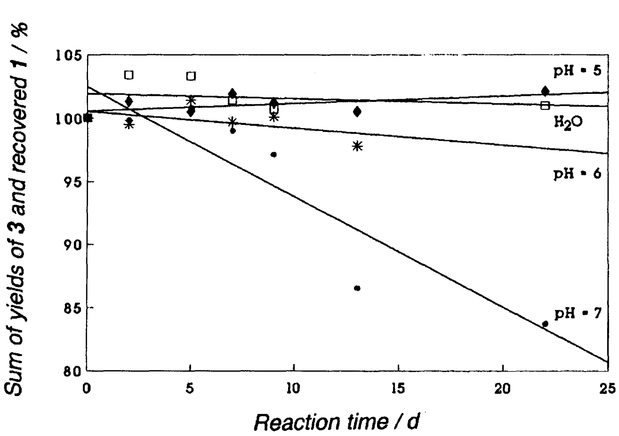


Fig. 5. Sum of the yields of the azo product **3** and the recovered diazonium ion **1** as a function of reaction time at various acidities.

That solution became, however, fairly acidic (pH<2). It is, therefore, likely that the base catalysis of the proton removal in the second step of the azo coupling (see below) is not as effective as in the other experiments performed in systems buffered at pH 5 to 7. The experiments with 3,7-di-*t*-butylnaphthalene-1-sulfonate (mentioned in the results section) are consistant with this interpretation. The sum of the concentrations of the azo product **3** and the residual dizaonium ion **1** decreases according to the sequence pH 5>6>7, as shown in Fig. 5. That decrease corresponds to the experience that the decomposition of the diazonium ions becomes more dominant at increasing pH from 4 to 10.[19)]

We believe that sodium 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (**6**), 3,7-diisopropyl- and 3,7-di-*t*-butyl naphthalene-1-sulfonate are interesting phase-transfer catalysts for azo coupling reactions, which cannot be carried out under conventional conditions.

The Influence of the Counter Anion on the Partition Coefficient (α) for the Diazonium Ion 1 in Dichloromethane/Water System. The partition of diazonium ions between an aqueous phase and an organic phase can be formulated with a partition coefficient (α). In the case of an arenediazonium tetrafluoroborate in the presence of an anionic catalyst in an aqueous/organic two-phase system, α is shown with the concentrations of the diazonium ion in both phases (Eq. 1).

$$\begin{aligned}\alpha &= [\mathrm{ArN_2^+}]_{\mathrm{org}}/[\mathrm{ArN_2^+}]_{\mathrm{aq}}\\ &= ([\mathrm{ArN_2^+BF_4^-}]_{\mathrm{org}}+[\mathrm{ArN_2^+Cat^-}]_{\mathrm{org}})/\\ &\quad ([\mathrm{ArN_2^+BF_4^-}]_{\mathrm{aq}}+[\mathrm{ArN_2^+Cat^-}]_{\mathrm{aq}}) \qquad (1)\end{aligned}$$

We determined the partition coefficients (α) for the diazonium ion **1** in a dichloromethane/water system at 20 °C with an equimolar amount of several catalysts (Table 4). Sodium salts of the following lipophilic

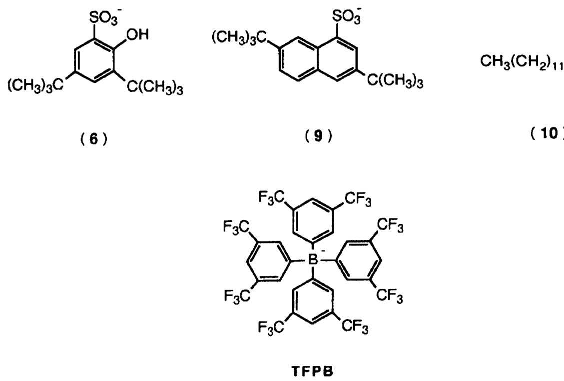
Table 4. Partition Coefficient (α) for Diazonium Ion 1 in Dichloromethane/Water System at 20 °C[a)]

Catalyst	α	$[\mathrm{ArN_2^+BF_4^-}]_{\mathrm{org}}$ / mol dm^{-3}	$[\mathrm{ArN_2^+Cat^-}]_{\mathrm{org}}$ / mol dm^{-3}
None	4.77×10^{-3}	1.98×10^{-7}	0
9	2.25×10^{-2}	1.98×10^{-7}	6.87×10^{-7}
6	6.67×10^{-2}	1.98×10^{-7}	2.31×10^{-6}
10	8.36×10^{-2}	1.98×10^{-7}	2.84×10^{-6}
TFPB	3.82×10^{1}	1.98×10^{-7}	3.81×10^{-5}

a) The overall concentrations of **1** and of catalyst are within the range of $(4.0-4.5)\times10^{-5}$ mol dm^{-3}.

organic acids were used as the catalysts: 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (**6**), 3,7-di-*t*-butylnaphthalene-1-sulfonate (**9**), dodecyl sulfate (**10**), and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) (Chart 2). The overall concentrations of the diazonium tetrafluoroborate **1** and of the catalyst were within the range of (4.0—4.5)$\times 10^{-5}$ mol dm^{-3}. The cmc (critical micellization concentration) of sodium dodecyl sulfate (**10**) was 8×10^{-3} mol dm^{-3};[20] i.e. there were no micelles under this conditions. The concentration of the diazonium ion **1** was measured in both phases.

Table 4 shows that without any catalyst only about 0.5% of **1** is partitioned in the dichloromethane phase, while, with catalysts **9**, **6**, and **10**, this value could be increased only by 2.2, 6.3, and 7.7%, respectively. On the other hand, with TFPB, 97.4% of the diazonium ion was partitioned in dichloromethane phase. The striking influence of TFPB to increase α can be explained by the characteristic structure of TFPB, in which a hydrophilic anionic center of the boron atom is, against hydration, symmetrically shielded by four bulky phenyl groups with strongly lipophilic trifluoromethyl groups. This is based on the analogy that the structural feature of well-known cationic PTC catalyst, such as tetraalkylammonium and phosphonium ions, whose positive center is also formally localized on nitrogen and phosphorus atoms, respectively, is shielded by four lipophilic alkyl groups in a tetrahedral way. In this aspect, the structure of the TFPB anion makes a strong contrast to that of organic sulfonate anions, whose anionic oxygen atoms are exposed into the surrounding media and provides a strongly hydrophilic center. The small, but obvious, increase in α with sulfonates **6**, **9**—**10** might be caused by an increased lipophilicity of the organic sulfonate anions, compared with that of tetrafluoroborate anion. As discussed above, the shielding and hydrophobic *t*-butyl groups of **6** and **9**, as well as the hydroxy group of **6**, to cause a better distribution of the negative charge of the sulfonate group of **6**, play important roles to increase α. However, the rate increase in the PTC azo coupling does not correspond to a first-order dependence on the α increase (see below). The large α value of dodecyl sulfate (**10**), compared with those of **6** and **9**, indicates that the hydrophobic effect of the long alkyl chain of **10** is probably more effective than the steric and hydrophobic effects of the two *t*-butyl groups of **6** and **9** to increase the partition coefficient (α).[21]

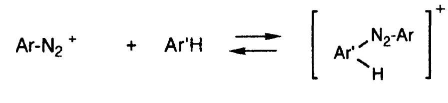


(**6**) (**9**) (**10**)

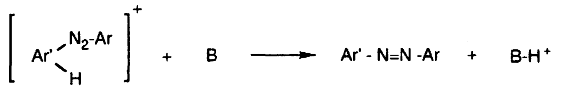
TFPB

Chart 2.

The Influence of Solvent Polarity and Counter Anions in the Azo Coupling Reactions of the Diazonium Ion 1 with *N,N*-Dimethylaniline (4) in Organic Phase. The azo coupling reaactions of arenediazonium ions with activated aromatic compounds in polar media proceed by the formation of a σ complex, followed by a proton transfer from the σ complex to a base[22] (Eqs. 2 and 3).



(2)



(3)

Some investigations concerning the solvent effects on the azo coupling rates in highly polar solvents have already been reported. In the azo coupling reaction of 4-toluenediazonium salts with *N,N*-dimethylaniline (**4**), a small solvent polar effect has been observed; the relative second-order rate constants in acetonitrile, water, and nitromethane are 1.0, 2.0, and 2.2, respectively, and no significant influence of counter anions (HSO_4^- or BF_4^-) was observed in acetonitrile and nitromethane.[23] The rate constants for the same reaction of 4-toluenediazonium tetrafluoroborate with **4** have been reported to change by 4.2 times in the transition from acetonitrile to dimethylacetamide, while the replacement of the unreactive 4-toluenediazonium ion by the more reactive 3- and 4-nitro derivatives with such solvents as nitromethane, acetonitrile, dimethylacetamide, and hexamethylphosphoric triamide increases the reactivity with respect to the solvent to 2—3 orders of magnitude. A linear correlation between the logarithms of these rate constants and the Gutmann's donor numbers (*DN*)[24] has indicated that the specific solvation of the diazonium cations plays a dominant role in the azo coupling in aprotic polar solvents.[25] A result of no significant influence of the solvent polarity has been found in the reaction of 3-nitrobenzenediazonium tetrafluoroborate with 1,3,5-trimethoxybenzene (**2**); the relative second-order rate constants in acetonitrile, methanol, nitromethane, and water are 1.0, 1.4, 1.1, and 2.4, respectively.[26]

In order to investigate the influence of the solvent polarity and of the structure of a counter anion on the rate of azo coupling, we measured the rate of the azo coupling of the diazonium ion **1** with *N,N*-dimethylaniline (**4**) to give 4-dimethylamino-4′-methoxyazobenzene (**5**) in organic solvents with different polarity, as well as in the presence of different kinds of lipophilic organic anions in dichloromethane.

The diazonium tetrafluoroborate **1** was dissolved with or without an equimolar amount of sodium salts of lipophilic organic anions **6**, **9**—**10** or TFPB as the catalyst in methanol, water-saturated dichloromethane, or dichloromethane, and coupled with a 100-fold excess of **4** under pseudo first-order reaction conditions at 20 °C. The coupling in methanol proceeded in first order for the concentration of **4** (Eq. 4), while the coupling in dichloromethane proceeded in second order for the concentration of **4**, where one mole of **4** served as the coupling component in the first step (coupling, Eq. 2) and another mole as the base for the second step (deprotonation, Eqs. 3 and 5):[6b,10a,10b]

$$\text{rate} = k_1[\mathbf{1}] = k_2[\mathbf{1}][\mathbf{4}] \tag{4}$$

where k_2 ($\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$)$=k_1$ (s^{-1})$/[\mathbf{4}]$ in methanol.

$$\text{rate} = k_1[\mathbf{1}] = k_2[\mathbf{1}][\mathbf{4}] = k_3[\mathbf{1}][\mathbf{4}]^2 \tag{5}$$

where k_2 ($\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$)$=k_1$ (s^{-1})$/[\mathbf{4}]$ and k_3 ($\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$)$=k_1/[\mathbf{4}]^2$ in dichloromethane.

Table 5 shows the rate constants for the reactions of the diazonium tetrafluoroborate **1** with **4** in methanol, dichloromethane and water-saturated dichloromethane. Table 6 shows the rate constants for the reactions of **1** with **4** in dichloromethane in the presence of **6**, **9**—**10** and TFPB.

In Table 5, the k_2 value for the reaction of **1** in dichloromethane (dielectric constant $\varepsilon_r=8.93$, $DN\approx0$) is more than ten-times larger than that in methanol ($\varepsilon_r=32.6$, $DN=19$). This indicates that, in a less polar solvent like dichloromethane, the diazonium ion **1** might be highly activated by a smaller amount of solvation. This is also indicated by the fact that a small amount of water in water-saturated dichloromethane (2 g of water in 1 dm^3 of dichloromethane;[27] 1.11×10^{-1} mol dm^{-3}, $\varepsilon_r=78.3$, $DN=18.0$) decreased the coupling rate by 25%. A similar and remarkable influence of saturated water has also been observed in the coupling reaction of benzenediazonium tetrafluoroborate with **4** in wet chloroform; i.e. with a small amount of water saturated in chloroform (0.6 g of water in 1 dm^3 of chloroform;[27] 0.33×10^{-3} mol dm^{-3}) the k_3 value was reduced to 1/30 of that in anhydrous chloroform ($\varepsilon_r=4.81$, $DN\approx0$).[6b]

Table 5. Rate Constants for the Reactions of Diazonium Tetrafluoroborate **1** with *N*,*N*-Dimethylaniline (**4**) in Organic Solvents at 20 °C

Solvent	k_1	k_2	k_3
	s^{-1}	$\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$
MeOH	3.85×10^{-5}	1.11×10^{-2}	
Wet CH_2Cl_2[a)]	3.71×10^{-4}	2.69×10^{1}	
Anhydrous CH_2Cl_2	5.30×10^{-4}	1.36×10^{-1}	3.47×10^{1}

a) Concentration of saturated water is 1.11×10^{-1} mol dm^{-3}.[27]

Table 6. Rate Constants for the Reactions of Diazonium Tetrafluoroborate **1** with *N*,*N*-Dimethylaniline (**4**) in Dichloromethane in the Presence of Lipophilic Organic Anions at 20 °C[a)]

Anion (catalyst)	k_1	k_3
	s^{-1}	$\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$
None	5.70×10^{-4}	3.35×10^{1}
6	4.26×10^{-4}	2.50×10^{1}
9	4.34×10^{-4}	2.55×10^{1}
10	5.94×10^{-4}	3.49×10^{1}
TFPB	2.71×10^{-3}	1.67×10^{2}

a) $[\mathbf{1}]=[\text{anion}]=4.03\times10^{-5}$ mol dm^{-3}.

In contrast to the data given in Table 4 that, compared with the tetrafluoroborate ion, lipophilic organic anions **6**, **9**—**10** are much effective to increase the solubility of the diazonium ion **1** in dichloromethane; the results given in Table 6 show that these sulfonate anions are not so effective to increase the rate of the coupling in dichloromethane, i.e. the k_3 values for **6** and **9** are rather smaller than that for the tetrafluoroborate ion. This can be explained by the formation of tight ion pairs of the diazonium ion with these sulfonate anions in nonpolar dichloromethane, and that the strong Coulombic attraction in the ion pair might reduce the reactivity of the diazonium ion in azo coupling. Therefore, the higher reactivity of the diazonium ion **1** with TFPB ($k_3(\text{TFPB})/k_3(\text{BF}_4)=5.0$, $k_3(\text{TFPB})/k_3(\mathbf{6})=6.7$) might be due to a loose ion-pair formation of the diazonium ion with the TFPB anion, as discussed above, whose anionic center is tetrahedrally shielded with bulky 3,5-bis(trifluoromethyl)phenyl groups. Similar effects of the loose ion-pair formation in the activation of diazonium ions have been discussed regarding the azo couplings of the benzenediazonium ion with **4** in chloroform ($k_3(\text{TFPB})/k_3(\text{BF}_4)=15.8$)[6b] and of 4-*t*-butylbenzenediazonium ion with **4** in dichloromethane ($k_3(\text{PF}_6)/k_3(\text{BF}_4)=4.0$).[10] In Table 6, however, dodecyl sulfate (**10**), which may form a closer ion pair than does the sulfonate **6** with its partially shielded negative charge, was slightly more effective to activate the diazonium ion **1** than was the sulfonate **6**. This indicates that both the looseness and the lipophilicity of the ion pair might be important factors in the effective azo coupling reaction under PTC conditions.

The Influence of Counter Anions and Additives in the Azo Coupling Reactions of the Diazonium Ion 1 with 1,3,5-Trimethoxybenzene (2) in Dichloromethane/Water System. We investigated the PTC azo coupling reactions of the diazonium tetrafluoroborate **1** with 1,3,5-trimethoxybenzene (**2**) to give 2,4,4′,6-tetramethoxyazobenzene (**3**) in the presence of a catalytic amount of sodium TFPB or sodium 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (**6**) in dichloromethane/water and in dichloromethane/solid systems.

Unless mentioned otherwise, all of the experiments were run under similar conditions as for the above cases with alkyl- and hydroxyl-substituted arenesulfonates; i.e., 2.25 mmol of the diazonium tetrafluoroborate **1** in 50 cm^3 of an aqueous phosphate buffer (pH=7.0) was mixed with a solution of 2.25 mmol of **2** with the sodium salt of TFPB (2.5 mol% or 5 mol%) or the sodium salt of **6** (2.5 mol% or 5 mol%) in 50 cm^3 of dichloromethane at 20 °C. 2,6-Dimethylpyridine (300 mol%) and 1-hexanol (5 wt% with respect to dichloromethane) were used as additives (see below). The yield of the product **3** was determined by capillary GC, as mentioned above (GC method), or by UV-vis spectroscopy (UV method) in a series of samples taken from the reaction system at various time intervals between 1.0 and 17.0 d; after sampling and diluting 0.2 cm^3 of the dichloromethane phase of the reaction mixture with dichloromethane containing excess 2,6-dimethylphyridine, the amount of the product **3** was measured spectrophotometrically by using a molar extinction coefficient of $\varepsilon=3050$ at 453 nm.

The results are shown in Fig. 6. The reaction rate constants ($k_1(s^{-1})$), the yields after 10 d calculated from k_1 (see below and experimental), and the final experimental yields are shown in Table 7.

As mentioned above, the yield of the azo product **3** with no catalyst after 12 d was only 0.26%. The yields in the reaction with 5 mol% of TFPB (Fig. 6, Lines 1 and 2) after 10 d were 18.5 and 20.5% by the GC and UV methods, respectively, while the yield in the reaction with 5 mol% of the sulfonate anion **6** after 10 d was 28.0% (Line 3); **6** was therefore more effective than was TFPB as a PTC catalyst under these conditions. Since the azo coupling of 1.8×10^{-3} mmol of the diazonium TFPB with 9.5×10^{-3} mmol of **2** in 3 cm^3 of dichloromethane did not proceed at all, the aqueous phase is essential for the above-mentioned PTC reaction (Lines 1 and 2).

On the other hand, the reaction with 2.5 mol% of TFPB in the presence of 300 mol% of 2,6-dimethylpyridine (Line 4) was much faster than that with 5 mol% of TFPB without 2,6-dimethylpyridine (Lines 1 and 2); after 7 d the yield was 64.3% in the reaction of Line 4, while the yield was 15.5% in the reaction of Line 2. In this case, when we postulate an azo coupling without any competitive decomposition of the diazonium ion and calculate the yield after 10 d from the initial rate constant (k_1) of 4.82×10^{-6} s^{-1}, the yield becomes 98% in the reaction of Line 4; in the actual case, however, 15% of the diazonium ion was found after 7 d, which means a 20% decomposition of the diazonium ion after 7 d. Since no decomposition of 1.8×10^{-3} mmol of the diazonium TFPB with 70 mol% of 2,6-dimethylpyridine in 3 cm^3 of anhydrous dichloromethane was observed, even after 18 h, the competitive decomposition of the diazonium ion might have occurred in the aqueous phase, or in a boundary phase in the two-phase system. Similarly, in solid(diazonium salt)/liquid(dichloromethane) system, the azo coupling reaction proceeded very fast in the presence of TFPB and 300 mol% of 2,6-dimethylpyridine (Line 5).

In contrast to the case of TFPB, the effect to accelerate the reaction rate by added 2,6-dimethylpyridine was not very significant in the case of the sulfonate anion **6**. In a one-point reaction with 2.5 mol% of **6** and 300 mol% of 2,6-dimethylpyridine after 7 d (indicated by **X** in Fig. 2), a 12.5% yield of **3** was obtained. Under the assumption that the yield is linearly related with catalyst concentration, a 12.5% yield with 2.5 mol% of **6** implies a 25.0% yield with 5.0 mol% of **6**, which is only 2.8% higher than the 22.2% yield in the reaction without 2,6-dimethylpyridine (Line 3).

By considering these results, we suppose that in reactions with TFPB (Lines 1 and 2) in a dichloromethane/water (pH=7.0) two-phase system, saturated water in the organic phase does not serve sufficiently as a base to transfer a proton from the σ-complex (Eq. 2) and/or a protonated azo product (see below) to the aqueous phase, while 2,6-dimethylpyridine functions well as a proton mediator from the organic phase to the aqueous phase (Line 4).[28] In the case of the sulfonate anion **6**, the amount of solvated water surrounding the sulfonate ion center is sufficient to transfter a proton from a protonated azo product to the aqueous phase, and no dimethylpyridine effect was observed. In other words, a proton transfer in the boundary phase might have occurred sufficiently only with saturated water in the case of **6** (line 3), but not sufficiently with water in the case of TFPB (Lines 1 and 2), since the amount of solvated water surrounding an ion pair of TFPB in the organic phase might be much less, compared with that surrounding an ion pair of **6**. This is also the reason why a highly *desolvated* and *loose* ion pair of the diazonium ion with TFPB is much more active than a *solvated* and *tight* ion pair of the diazonium ion with **6** in the reaction under the influence of 2,6-dimethylpyridine, in which the first coupling step (Eq. 2) is rate-limiting.

One experimental result which supports this idea was the rate acceleration of the azo coupling with 2.5 mol% of TFPB and 5.0 wt% of 1-hexanol but *without* 2,6-dimethylpyridine, where the yield of **3** (22.6% after 7 d, Line 6) was higher than the yield (12.5% after 7 d, **X** in Fig. 6) in the one-point reaction with 2.5 mol% of **6** and 300 mol% of 2,6-dimethylpyridine. 1-Hexanol might be effective to accelerate a proton transfer in the boundary phase.

The spectrum of the dichloromethane solution of the reaction mixture in the reaction with TFPB after 17 d (Line 2) showed that the produced azo compound is protonated and ion-paired with TFPB in this reaction mixture ($\lambda_{max}=506$ nm), and that the addition of

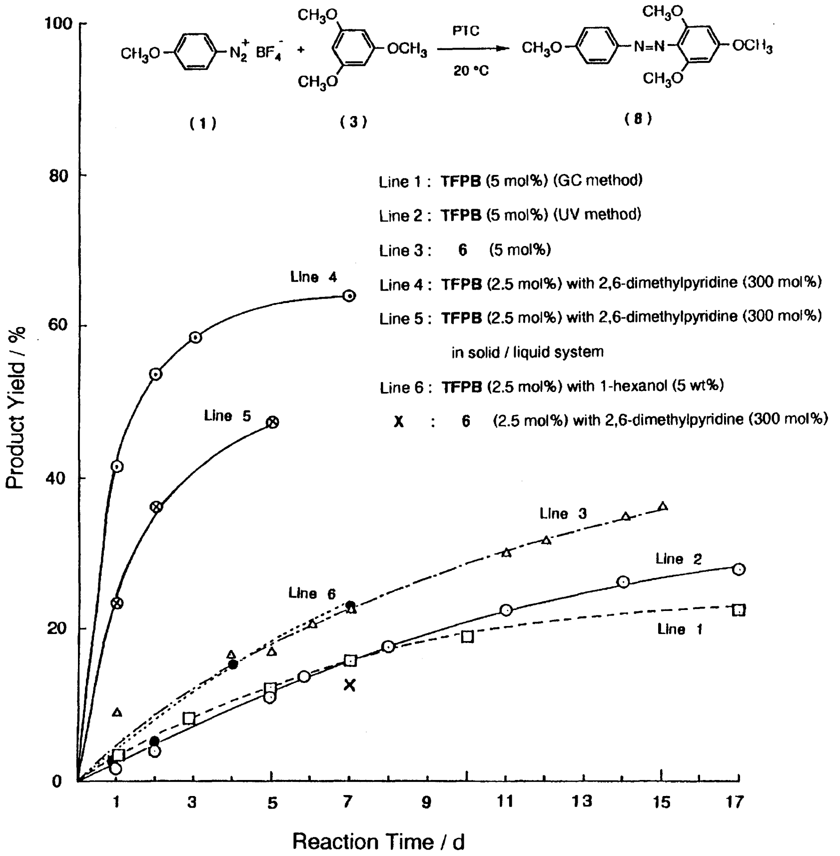


Fig. 6. The azo coupling reactions of the diazonium ion **1** with 1,3,5-trimethoxybenzene (**2**) in the presence of TFPB and 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (**6**) in dichloromethane/water (pH=7.0) system at 20 °C.

Table 7. Results of Azo Coupling Reactions of 4-Methoxybenzenediazonium Tetrafluoroborate (**1**) with 1,3,5-Trimethoxybenzene (**2**) in the Presence of Sodium Salts of TFPB and 3,5-Di-*t*-butyl-2-bydroxybenzenesulfonate (**6**) in Dichloromethane/Water System[a)]

Line No. in Fig. 6	Catalyst (Na salt)		Duration of experiments	Yield after 10 d	Final yield of **3**		Rate constant k_1
	mol%		d	%	%	(days)	s^{-1}
1	TFPB	(5.0)[b)]	17.0	22.5	22.0	(17.0)	2.95×10^{-7}
2	TFPB	(5.0)[c)]	17.0	20.5	28.0	(17.0)	2.66×10^{-7}
3	**6**	(5.0)[b)]	15.0	26.7	35.5	(15.0)	3.60×10^{-7}
4	TFPB	(2.5)[c,d)]	17.0	98.4	64.3	(7.0)	4.82×10^{-6}
5	TFPB	(2.5)[c,e)]	17.0	90.4	47.5	(5.0)	2.71×10^{-6}
6	TFPB	(2.5)[c,f)]	17.0	32.4	22.6	(7.0)	4.54×10^{-7}

a) Diazonium salt **1** (2.25 mmol) and **3** (2.25 mmol) in 50 cm^3 dichloromethane with 50 cm^3 of water (pH=7.0) at 20 °C. b) GC Method. c) UV Method. d) With 2, 6-dimethylpyridine (300 mol%) in liquid/liquid system. e) With 2,6-dimethylpyridine (300 mol%) in solid/liquid system. f) With 1-hexanol (5 wt% with respect to dichloromethane).

an excess amount of 2,6-dimethylpyridine to this solution gives a spectrum of the liberated azo compound **3** (λ_{max}=442 nm).

A similar spectrum of the solution of the protonated azo compound **3′** ion-paired with TFPB in dichloromethane with λ_{max} at 506 nm (ε=39000) and 327 nm (ε=5300) could be prepared independently by mixing a dichloromethane solution of the azo compound **3** with λ_{max} at 442 nm (ε=3200) and 349 nm (ε=13700) with a dichloromethane solution of equimolar oxonium TFPB, which was prepared in situ from sodium TFPB in dichloromethane and 0.2 mol dm^{-3} hydrochloric acid by an exchange of a sodium ion with an oxonium ion (Chart 3).[6c,6e,7a)]

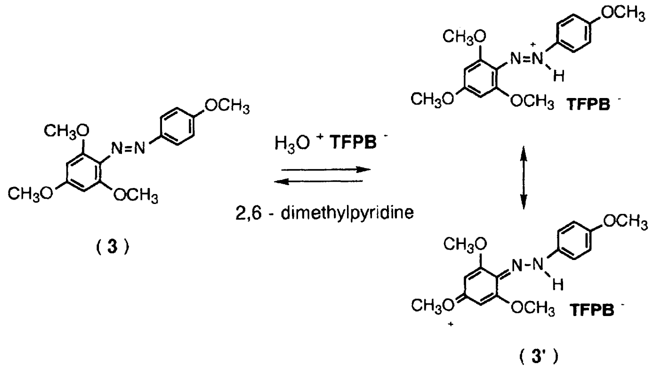


Chart 3.

This protonated azo compound **3**′ might have served as a poison to retard the PTC reaction, since **3**′ is a highly lipophilic cationic species with TFPB, and might hinder the incorporation of the diazonium ion **1** from the aqueous phase into the organic phase, which is an essential process for the azo coupling under PTC conditions. This idea was further supported by the following results concerning reactions of 1.8×10^{-3} mmol of the diazonium ion **1** and 1.8×10^{-3} mmol of TFPB with 9.5×10^{-3} mmol of **2** in 3 cm^3 of anhydrous dichloromethane at 25 °C.

In the reaction of the diazonium TFPB with **2** in the presence of excess 2,6-dimethylpyridine in anhydrous dichloromethane, a fast increase in the free azo compound **3** ($\lambda_{\text{max}}=442$ nm) was observed while following the change in the UV-vis spectrum of the reaction mixture; as shown above, in the same reaction of the diazonium TFPB in anhydrous dichloromethane without 2,6-dimethylpyridine, no change in the spectrum of the reaction mixture after 1 d indicated no azo coupling. The azo coupling without 2,6-dimethylpyridine in dichloromethane proceeded only when the dichloromethane phase was contacted with the aqueous phase to transfer a proton produced in the azo coupling from the organic phase into the aqueous phase.

In a time-course of the spectral change of dichloromethane solution of the diazonium TFPB with **2** in the presence of 70 mol% of 2,6-dimethylpyridine, a very slow and small increase of the protonated azo compound **3**′ ($\lambda_{\text{max}}=506$ nm) was indicated in 21 d. The addition of excess 2,6-dimethylpyridine to this reaction mixture induced a hypsochromic change in the spectrum of the reaction mixture ($\lambda_{\text{max}}=442$ nm of the liberated **3**) as well as a drastic increase in the rate of the azo coupling reaction.

In conclusion, a comparison of the partition coefficients (α) of the diazonium ion **1** with a series of lipophilic organic anions in a dichloromethane/water two-phase system indicated that the distinctive symmetrical structure of TFPB, whose anionic center is surrounded by highly lipophilic and bulky 3,5-bis(trifluoromethyl)phenyl groups, is an essential factor for the remarkably high α for the diazonium ion **1** ion-paired with TFPB. The looseness and tightness of the ion pairs of the highly desolvated diazonium ion in a nonpolar media, such as dichloromethane, might be one of the most significant factors for activating the diazonium ion in the rate-limiting azo coupling (Eq. 2); in the azo coupling reactions under the conditions of rate-limiting deprotonation in dichloromethane/water two-phase system, however, the amount of saturated water and/or additives in the dichloromethane phase, which serve as a base for deprotonation (Eq. 3), becomes a most influential factor for an effective azo coupling under PTC conditions.

Experimental

Materials: 4-Methoxybenzenediazonium tetrafluoroborate (**1**) was prepared by the usual method.[29] Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB)–water (2/5),[6d,6f] which is commercially available from DOJIN Laboratory, was used.

Spectra: The UV-vis spectra were measured on Shimadzu UV-240 and Hitachi U-3200 spectrometers. Cells were kept at 20.0±0.1°C with Julabo F10- and VL-thermostates and a Komatsu-Yamato Coolnics CTR-220.

PTC Azo Coupling Reactions: 4-Methoxybenzenediazonium tetrafluoroborate (**1**) (2.25 mmol) and catalyst (0.1125 mmol, 5 mol%) were dissolved in 40 cm^3 water. A phosphate buffer (6.5 cm^3, pH=7, 0.4 $\text{mol}\,\text{dm}^{-3}$) was added and made up to 50 cm^3. This solution was mixed with 50 cm^3 of a dichloromethane solution containing 1,3,5-trimethoxybenzene (2.25 mmol) and 250 mg dibutylphthalate as internal standard in a black Erlenmeyer flask (200 cm^3). The flask was maintained at 20.0±0.1°C and the mixture was agitated with a magnetic stirrer at about 1200 r.p.m. After appropriate periods, the stirring was stopped; after phase separation, 0.1 cm^3 of the organic phase was removed and diluted with dichloromethane to 0.7 cm^3 for a GC analysis. Gas chromatograms were run on a Hewlett-Packard HP-5880A chromatograph (level 4) with a methylsilicone capillary column (OV 101, 0.2 mm, 12.5 m). The injector temperature was 270 °C, that of the FID dectector 300 °C. The heating rate of the column was 25 $°\text{C}\,\text{min}^{-1}$ from 140 to 240 °C. 1,3,5-Trimethoxybenzene (**2**), dibutyl phthalate, and the azo product **3** were separated cleanly. For further details, accuracy and reproducibility see Murer's Ph. D. thesis.[30]

The **solubility** of 4-methoxybenzenediazonium tetrafluoroborate (**1**) in dichloromethane and of 1,3,5-trimethoxybenzene (**2**) in water was determined spectrophotometrically after measuring the respective molar extinction coefficients.

Recovered diazonium ion was determined by adding a sample to a solution of R-acid (in excess). The formed azo compound was measured spectrophotometrically at 509 nm at pH=2 (molar extinction coefficient $\varepsilon=20900$).

Syntheses. 2,4,4′,6-Tetramethoxyazobenzene (3): 845 mg (5 mmol) 1,3,5-trimethoxybenzene (**2**) was dissolved in 200 cm^3 ethanol. A solution of 1.11 g (5 mmol) 4-methoxybenzenediazonium tetrafluoroborate in 50 cm^3 water was added. During the coupling reaction ethanol was added from time to time to keep all compounds dissolved. The reaction mixture was kept in the dark for 12 d and then extracted with dichloromethane. The organic phase was purified using column chromatography on silica gel 60 (Merck). The red azo compound **3** was eluted from the column with dichloromethane/toluene/ethyl acetate (7/2/1) and recrystallized from hexane/ethanol. Yield: 230 mg (15%), mp 102.5 °C. UV-vis 352 nm (17750); 453 nm (3050). For IR and NMR see Murer's Ph. D. thesis.[30)]

Sodium 1,3,5-Trialkyl- and Pentamethylbenzenesulfonates: 0.25 mol of the alkylated benzene was dissolved in 70 cm^3 dichloromethane. At 0 to 5 °C 40.8 g chlorosulfuric acid was added dropwise with stirring during one hour. Stirring was then continued and the reaction mixture was no longer cooled. After 10 h at room temperature the solution was poured onto ice. Aqueous 10% sodium hydroxide was added until the solution was alkaline. The sodium sulfonate was precipitated by the addition of an aqueous 20% sodium chloride solution. After filtration and drying, the precipitate was recrystallized from ethanol/water. The test for chloride (Beilstein) was negative.

Sodium 1- and 2-Naphthylmethanesulfonate were synthesized from 1- and 2-methylnaphthalene, respectively, by photolytic bromination and nucleophilic substitution of the bromomethyl derivative with sodium sulfite following a procedure for the 1-isomer.[31)]

Sodium 3,5-di-*t*-Butyl-2-hydroxybenzenesulfonate (6) was synthesized following Brändström.[18)]

Sodium 3,5-di-*t*-Butyl-2-hydroxyphenylmethanesulfonate (7) was synthesized starting from 2,4-di-*t*-butylphenol, in analogous fashion to the synthesis described by Sinhababu and Borchardt[32a)] and Bunton and Halevi.[32b)] For details see Murer's Ph. D. thesis.[30)] The methyl derivative (**8**) was synthesized according to Organikum.[31)]

Sodium 3,7-Dialkylated Naphthalenesulfonates were synthesized from the respective 2,6-dialkylnaphthalenes by sulfonation with chlorosulfuric acid in 1,2-dichloroethane, isolation of the monohydrate of the 4-sulfonic acid and formation of the sodium salt with sodium carbonate, following procedures published by Menard et al.[33a)] and van Bekkum et al.[33b)] Both sodium salts contain **1** mole of water of crystallization. Details of synthesis, spectral, and analytical data have been published elsewhere.[30)]

Partition Coefficient α: An aqueous solution of 4-methoxybenzenediazonium tetrafluoroborate (**1**) with an equimolar amount of the sodium salt of organic anions **6**, **9**—**10** and TFPB and the same volume of dichloromethane are mixed. The overall concentrations of **1** and sodium salts are within the range of (4.0—4.5)$\times 10^{-5}$ mol dm^{-3}. The two phases of dichloromethane/water (1/1) were equilibrated by stirring vigorously for 3 h at 20.0 °C. After separation of the phases, the concentration of the diazonium ion in each phase was determined by adding a sample to a solution of excess *N,N*-dimethylaniline (**4**) (organic phase) and excess *R*-acid (aqueous phase). The formed azo compounds were measured by spectrophotometry at 509 nm at pH=2.0 (molar extinction coefficient ε of the azo compound obtained from *R*-acid is 20900) and at 410 nm in dichloromethane (ε of 4-dimethylamino-4′-methoxyazobenzene (**5**) is 30000).

Kinetic Measurements of Azo Coupling Reactions. Reaction with *N,N*-Dimethylaniline (4). Two solutions of the diazonium tetrafluoroborate **1** and *N,N*-dimethylaniline (**4**) with or without an equimolar amount of sodium salt of organic anions (**6**, **9**—**10** and TFPB) in an organic solvent (methanol, water-saturated or anhydrous dichloromethane) were prepared in such a way that a mixture of these two solutions would result in an azo coupling reaction with a product concentration which gives an absorption of about 1.0 at the end point. The solution of **4** was 100-fold more concentrated than that of **1**, i.e. pseudo first-order reaction conditions.

To 1.0 cm^3 of 4×10^{-3} mol dm^{-3} solution of **4** in a 1cm quartz cell were added 1.0 cm^3 of 4×10^{-5} mol dm^{-3} solution of **1** and 1.0 cm^3 of the same solvent, and the reaction was followed by the increase in the absorption maximum (410 nm) of the reaction product, 4-dimethylamino-4′-methoxyazobenzene (**5**), with the lapse of time at the temperature kept at 20.0±0.1°C. Thus the pseudo first-order rate constant k_1(s^{-1}) was obtained by the following equation:

$$k_1 \times t = \ln[A_\infty/(A_\infty - A_t)]$$
$$k_2 = k_1/[\mathbf{4}]$$

where A_∞ and A_t denote the optical densities at an infinite time and at time *t*, respectively. The coupling in dichloromethane proceeded in second order for **4**. Thus, the third-order rate constant (k_3) was obtained as follows:

$$k_3 = k_1/[\mathbf{4}]^2$$

Reactions with 2,3,5-Trimethoxybenzene (2) in Dichloromethane/Water System. All experiments were run under similar conditions, as described above. Diazonium tetrafluoroborate (**1**) (2.25 mmol) in 50 cm^3 of an aqueous phosphate buffer (pH=7.0) was mixed with a solution of 2.25 mmol of **3** with sodium salt of TFPB (2.5 mol% or 5.0 mol%) or sodium salt of 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (**6**) (2.5 mol% or 5 mol%) in 50 cm^3 dichloromethane. Reactions were run in 200 cm^3 round-bottomed flasks at a temperature kept at 20.0±0.1°C; the two-phase reaction mixture was stirred with a power stirrer with a stirring speed of more than 1000 r.p.m. 2,6-Dimethylpyridine (300 mol%) and 1-hexanol (5 wt% with respect to dichloromethane) were used as additives. The reaction was followed by capillary gas chromatography, as described above (GC method), or by a UV method: The dichloromethane solution (0.2 cm^3) of the reaction mixture was diluted with dichloromethane containing excess 2,6-dimethylpyridine, and the amount of the azo product **3** in the diluted solution was determined at the absorption maxium at 453 nm (ε=3050) in dichloromethane. The kinetic results are shown in Fig. 6 and Table 7.

The yields after 10 d (Table 7) were calculated based on the slope taken from the linear regression, in which the elapsed reaction time (in seconds) is plotted against $\ln[P_\infty/(P_\infty - P_t)]$ ($P_\infty = D_0$), where D_0, P_t, and P_∞ denote the starting concentration of the diazonium ion and the product concentration at time$=t$ and ∞. This procedure is a method used to compare the efficiency of the various catalytic systems on the basis of yield. To obtain a good linear regression for calculating the starting reaction rates, only the first few points were taken. It is therefore possible that the calculated yield after 10 d is higher than the effective value at the end of the experiment, because of the decreasing slope at the end of the experiment due to the diazo decomposition.

Reactions of 4-Methoxybenzenediazonium (1)

TFPB in Anhydrous Dichloromethane. The mixture of 0.02 mmol of the diazonium tetrafluoroborate (**1**) and 0.027 mmol of sodium TFPB in 20 cm^3 of dichloromethane was sonicated with a BRANSONIC 42 ultrasonic cleaner (45 kHz) for 1 min. After precipitated sodium tetrafluoroborate was separated, the dichloromethane solution of the diazonium TFPB was diluted to 9.0×10^{-4} $\mathrm{mol\,dm^{-3}}$ with anhydrous dichloromethane. This diluted solution was used for the reactions with **2** in the presence/absence of 2, 6-dimethylpyridine.

Formation of the Protonated Azo Compound 3′ in the Reaction of the Azo Compound 3 with Oxonium TFPB in Dichloromethane. Oxonium TFPB solution (1.0×10^{-4} $\mathrm{mol\,dm^{-3}}$) in dichloromethane was prepared in situ by shaking a mixture of 5 cm^3 of 1.0×10^{-4} $\mathrm{mol\,dm^{-3}}$ dichloromethane solution of sodium TFPB and 5 cm^3 of 0.2 $\mathrm{mol\,dm^{-3}}$ hydrochloric acid for 1 min (exchange of sodium ion with oxonium ion).[6c,6e,7a] When this dichloromethane solution of oxonium TFPB was mixed with 1.0×10^{-4} $\mathrm{mol\,dm^{-3}}$ dichloromethane solution of the azo compound **3**, the electronic spectrum of **3** with absorption maxima at 442 nm (ε=3200) and 349 nm (ε=13700) changed to the spectrum of the protonated azo compound **3′** with absorption maxima at 506 nm (ε=39000) and 327 nm (ε=5300) in dichloromethane.

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