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Fluorinated Tetraarylborates as Anionic Phase-transfer Catalysts: An Example of Molecular Design of Functional Fluoroaromatics

Junji ICHIKAWA, Hiroshi KOBAYASHI, and Takaaki SONODA

Dedicated to Professor Otohiko Tsuge on the occasion of his retirement

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB), a highly lipophilic fluoroaromatic borate ion which is remarkably stable under acid and oxidative conditions, was designed as an anionic phase-transfer catalyst, whose function is to transfer cationic species such as diazonium and oxonium ions in reactive form of ion pair from an aqueous (or solid) phase into a nonpolar organic phase and to promote catalytically the electrophilic reactions in two-phase systems. Some effective examples of anionic phase-transfer catalysis (PTC) with TFPB were demonstrated in the diazo coupling, the Friedel-Crafts alkylation, the nitrosation (*in situ* diazo coupling), the acid-mediated hydrolysis of esters, and the redox reactions with methylviologen in the liquid membrane system. Kinetic investigations of these PTC reactions clearly indicated that the enhanced reactivities of the cationic species and the specificities of the electrophilic reactions were due to the dehydration of such cationic species ion-paired with TFPB in nonpolar organic phase.

Introduction

Scientific knowledge and industrial applications of phase-transfer catalysis (PTC) have expanded greatly during the last 15 years, and future chemical manufacturing processes will more incorporate PTC system because of its practical simplicity and economic advantages. [1] 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. Most of published works on PTC, however, have dealt only with the transfer of anionic reagents in nucleophilic or base-mediated reactions using quaternary ammonium or phosphonium salts, or crown ethers in liquid-liquid or liquid-solid systems. Opposite to the cation-catalyzed PTC, anion-catalyzed PTC may also proceed, if a suitable anionic catalyst is provided to transfer cationic reagents from an aqueous (or solid) phase and promote electrophilic reactions in nonpolar organic phase (Fig. 1).

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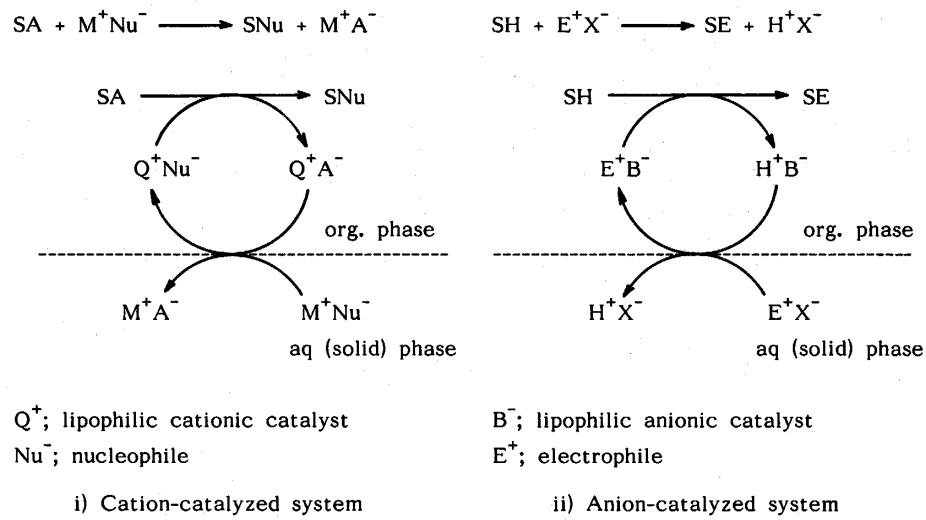


Fig. 1 Catalytic cycles of phase-transfer catalysis.

A few examples of transferring cationic species in PTC systems have been reported so far in the reactions of arenediazonium ions, although such attempts have not always been successful. [2] This is due to the lack of an efficient anionic catalyst for this purpose. We directed our attention to tetraphenylborate (TPB) ion as a possible anionic phase-transfer catalyst, in which hydrophilic anionic center of boron atom is shielded by four lipophilic phenyl ligands in a tetrahedrally symmetric array. This is on the analogy of the structural feature of tetraalkylammonium ion, whose positive center is formally localized on nitrogen and shielded by lipophilic alkyl groups similarly in a tetrahedral way (Fig. 2). In this respect, the structure of TPB anion makes a strong contrast to those of ordinary organic anions such as conjugate bases of carboxylic and sulfonic acids, whose anionic oxygen atoms are exposed into the surrounding medium and provides a strongly hydrophilic center.

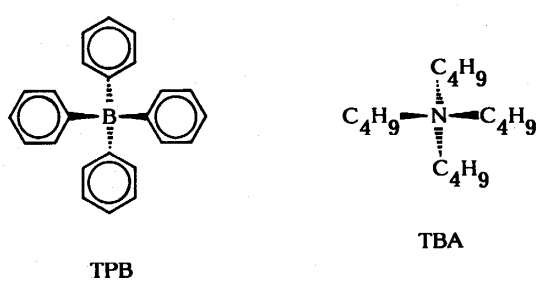
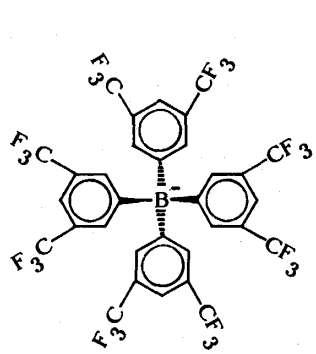


Fig. 2 Tetraphenylborate and tetrabutylammonium ions.

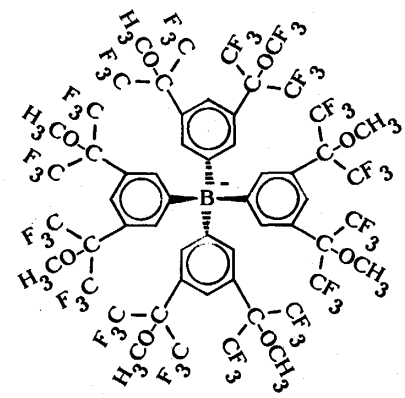
However, TPB anion is highly susceptible to the decomposition under acid and oxidative conditions, [3] and its solubilities in nonpolar organic solvents is not always satisfactory. This is a serious disadvantage of TPB for use in the anionic PTC, because in the anion-catalyzed PTC process the reaction is generally acid-mediated and the leaving group in the reaction is a proton

or protonated species. Our efforts were, therefore, focussed on improving the drawback of the chemical instability and, at the same time, attaining a higher lipophilicity by introducing trifluoromethyl groups on the phenyl rings of TPB.

We present here a review of our recent studies on the preparations and the properties of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) and tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]borate (Borate I) anions [4] (Fig. 3), and some effective examples of PTC reactions promoted by these arylborate ions.



TFPB



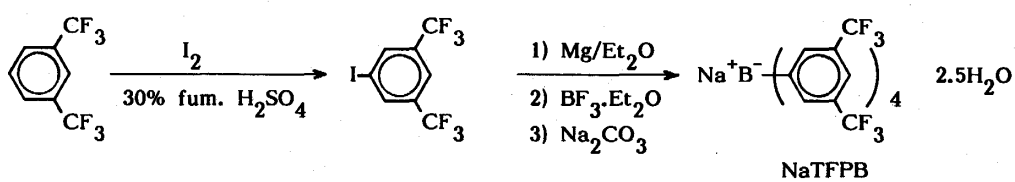
Borate I

Fig. 3 Trifluoromethyl-substituted tetraarylborates: Tetrakis[3,5-bis (trifluoromethyl)phenyl]borate (TFPB) and tetrakis [3,5-bis(1, 1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]borate (Borate I) anions.

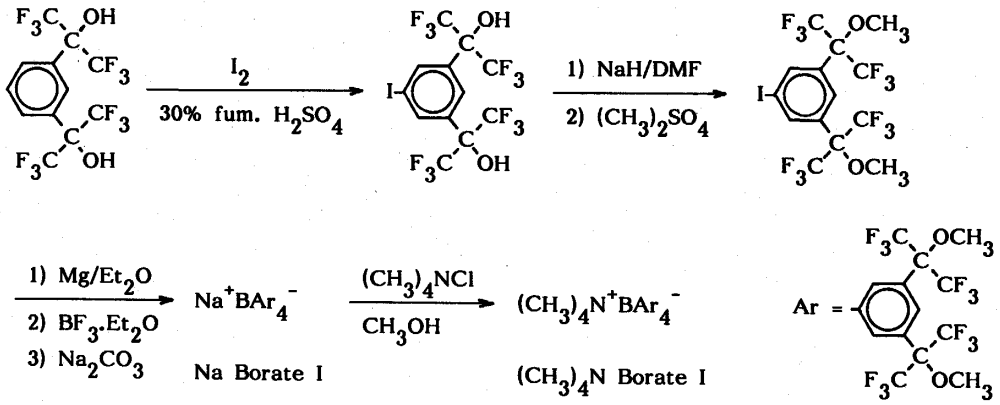
Preparations and Properties of TFPB and Borate I

Synthesis of TFPB and Borate I were performed according to Schemes 1 and 2, respectively, in satisfactory yields.

The substitution with trifluoromethyl groups induced drastic changes in the solubility of TPB in nonpolar organic solvents and the durability under acid and oxidative conditions. Sodium TPB was readily soluble in water but much less soluble in hydrophobic organic solvents, while sodium TFPB and sodium Borate I were practically insoluble in water but remarkably soluble in organic solvents such as dichloromethane, chloroform, benzene, and toluene. Interestingly, tetramethylammonium Borate I was fairly soluble even in dibromotetrafluoroethane



Scheme 1



Scheme 2

Table 1. Solubilities of TFPB and Borate I in hydrophobic organic solvents

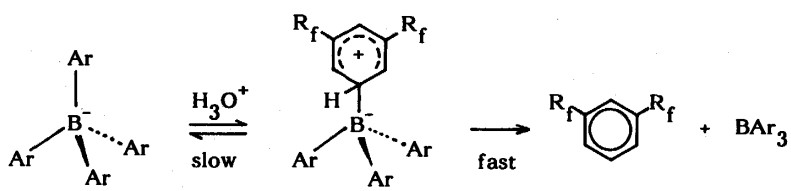
Solvent	Dielectric Constant	TFPB mol dm^{-3}	Borate I mol dm^{-3}
Dichloromethane	8.93 (25℃)	7.5×10^{-3} a)	8.6×10^{-3} a)
Chlorobenzene	5.62 (25℃)	2.0×10^{-4} a)	2.6×10^{-4} a)
Toluene	2.38 (25℃)	1.2×10^{-4} a)	3.2×10^{-4} a)
$CBrF_2CBrF_2$	2.34 (25℃)	— a) b)	1.3×10^{-4} a)
Hexane	1.88 (20℃)	7.0×10^{-6} c)	8.5×10^{-6} c)

a) sodium salt. b) less than 1.6×10^{-5} mol dm^{-3}. c) tetramethylammonium salt.

(DF-114B2) and hexane (Table 1).[4]

Comparisons of the proton-mediated decomposition rates of tetraarylborate ions in dichloromethane-aqueous sulfuric acid two-phase systems indicate that TPB anion decomposed immediately even in the two-phase system containing such diluted sufuric acid as 0.5 mol dm^{-3}, while trifluoromethyl-substituted arylborate ions were relatively stable under such acid condi-

Table 2. First-order rate constants of acid-decomposition of tetraarylborates in CH_2Cl_2-aq H_2SO_4 two-phase system.



(R_f = H, $C(CF_3)_2OCH_3$, CF_3)

H_2SO_4 Concn./ mol dm^{-3}	Decomposition Rate Consts. /s^{-1}		
	TPB	Borate I	TFPB
0.5	a)	1.45×10^{-4}	b)
3.0	a)	5.23×10^{-4}	b)
5.1	a)	8.71×10^{-4}	b)
10.3	a)	a)	0.96×10^{-4}

a) immediately decomposed. b) stable to be intact.

tions (Table 2). Especially TFPB was durable enough even in the system containing 5.1mol dm^{-3} sulfuric acid. The remarkable stability of TFPB may be due to the strong electron-withdrawing ability of trifluoromethyl group (Hammett's σ_m of CF_3=0.44), which retards more effectively the proton attack on the *ipso* carbon atom of the aryl ring compared with 1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl group (σ_m of $C(CF_3)_2OH$=0.35).

Similarly the oxidative degradation of TPB occurred easily under aerated conditions, while TFPB remained intact even after 22 hr when its dichloromethane solution was stirred vigorously with 10% aqueous nitrous acid or 10% aqueous hypochlorite and when treated with twice molar amounts of bromine in a chloroform solution at room temperature. [5]

Diazo-coupling Reactions in Two-phase Systems

Diazo-coupling reactions of arenediazonium ions with various couple components in dichloromethane-water two-phase systems were demonstrated to proceed smoothly in the presence of a catalytic amount of TFPB, where the diazonium ions in aqueous phase were incorporated in the form of ion pair with TFPB into the organic phase and a proton liberated in the diazo coupling was released out into the aqueous phase to recycle the PTC system (Fig. 4). [6]

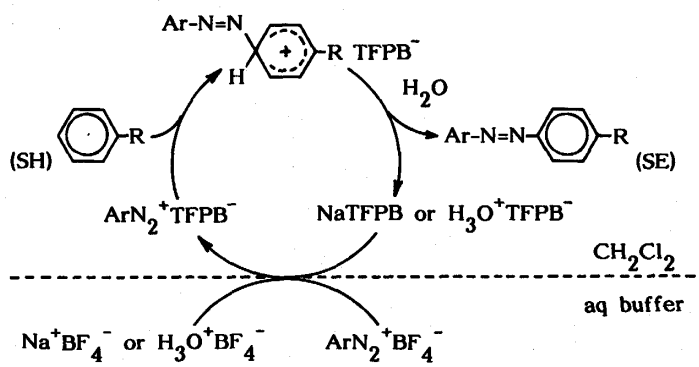
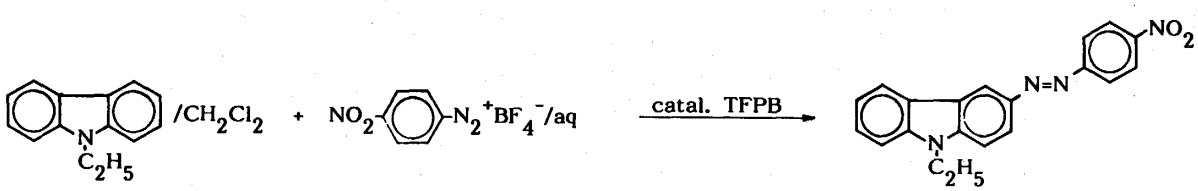
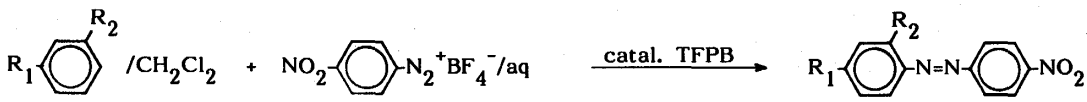


Fig. 4 Catalytic turnover in diazo coupling under PTC conditions.

The diazonium ions incorporated into the organic phase became highly reactive due to the dehydration from the cation, which was obviously indicated in the successful diazo-coupling reactions of *p*-nitrobenzenediazonium ions with *N*-ethylcarbazole and substituted anisole derivatives (Schemes 3 and 4, and Table 3). The coupling with such couplers in homogeneous aqueous



Scheme 3



Scheme 4

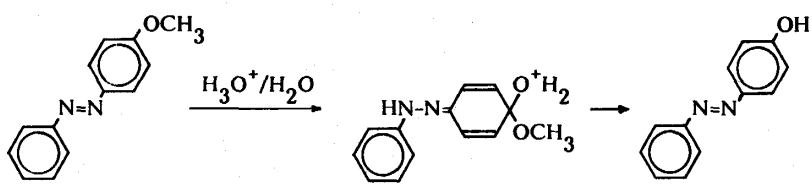
Table 3. Phase-transfer catalyzed diazo-coupling reactions[a]

Entry	R_1	R_2	Time / h	Yield[b] / %
1	C_6H_5NH	H	2	76
2	$C_6H_5(CH_3)N$	H	2	85
3[c]	CH_3O	H	48	10
4	CH_3O	CH_3	12	50
5	CH_3O	CH_3O	2	85

a) 7 mol % of TFPB was added into a 1 : 1 coupler-diazonium salt mixture in aq buffer-CH_2Cl_2 two-phase system at 25℃. b) isolated yield. c) 10 times molar amounts of coupler component was added.

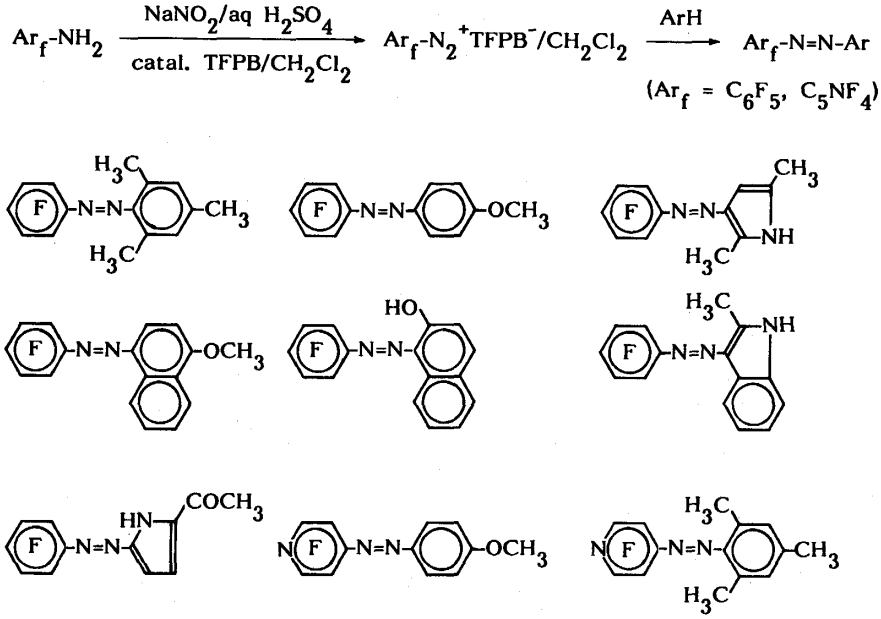
system was very sluggish; anisole was quite less reactive in the normal homogeneous system and the coupling of *p*-nitrobenzenediazonium ions with *N*-ethylcarbazole in acetic acid gave the product only 5% after 48 hr, while more than 80% yield of the product was produced after 3-hr in the two-phase system using TFPB.

Another effective point of the diazo coupling in the two-phase system was the increased specificity of the diazo coupling; demethylation of aryl methyl ether by hydrolysis was always accompanied in the homogeneous aqueous system, while it was completely avoided due to the dehydration in the organic phase (Scheme 5). [7]



Scheme 5

The anionic PTC with TFPB was applied to the *in situ* diazo-coupling reactions of perfluoroarenediazonium ions. [8] Diazotization of pentafluoroaniline and 4-aminotetrafluoropyridine must be done normally in strong acid such as 80% hydrofluoric acid, which is necessary owing to their low basicities and to avoid the nucleophilic substitution of fluorine atom of the labile perfluoroarenediazonium ions under aqueous conditions. [9] The following examples showed that the PTC system with TFPB (Scheme 6) was quite suitable for the *in situ* diazo coupling and related reactions of unstable diazonium ions under simple and mild conditions (Scheme 7). [10]

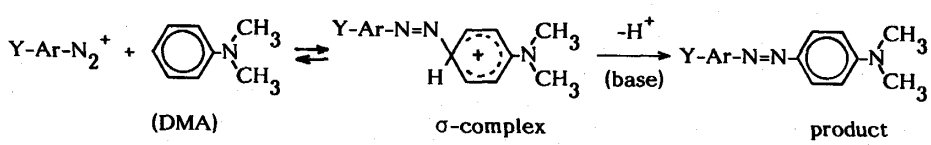


Scheme 6

Scheme 7

Kinetic Investigation on Diazo-coupling Reactions of Arensdiazonium TFPB in Nonpolar Organic Solvents

The effect of solvent polarity on the reaction rate depends in part on the charge density in the initial state relative to that in the transition state. In diazo coupling the starting diazonium ion has a high charge density but in the transition state (the σ-complex in Scheme 8) the charge is already dispersed, then a polar solvent should stabilized the starting diazonium ion more than the transition state. The result would be an increase in the activation energy and a decrease in the reaction rate. The diazo coupling of arenediazonium ions is known to proceed *via* a two-step S_E2 mechanism with a σ-complex intermediate (Scheme 8),[11] where the overall reaction rate is given by $d[\text{Product}]/dt = k_{obs}[\text{Y-ArN}_2^+ X^-]$.



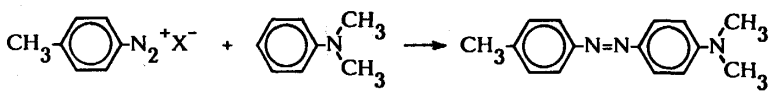
Scheme 8

In polar solvents such as water, alcohol, and acetic acid, the first σ-complex formation step becomes the rate determining one, and observed rate constant, k_{obs} is proportional to the concentration of a coupler (*N,N*-dimethylaniline (DMA) in this case). In a nonpolar solvent, on the other hand, the second deprotonation step from the σ-complex becomes the rate-determing one, since the basicity of the solvent is so low that an additional base is necessary for deprotonation. In the case of the diazo coupling with DMA in nonpolar solvents, k_{obs} shows a second-order dependence on the concentration of DMA, where one DMA serves as a coupler and the other as a base for deprotonation. [6]

The change of the rate-determinig step can be confirmed also by measuring the kinetic isotope effect on the rate constant of the diazo coupling with *N,N*-dimethylaniline-2,4,6-d_3. The rate constant ratio (the primary kinetic isotope effect), k_H/k_D, was known to become 1.96 when the deprotonation step was rate-determining in the reaction of *p-t*-butylbenzenediazonium ions with DMA in 1,2-dichloroethane, [12] while there is no primary kinetic isotope effect (k_H/k_D =1) when the first σ-complex-formation step is rate-determining.

A variety of substituted benzenediazonium TFPB dissolved in organic solvents of a wide range of polarities are suitable for the investigation of the solvent effect on the diazo-coupling reactions. Measured rate constants of the diazo coupling of *p*-methylbenzenediazonium tetrafluoroborate and its TFPB salt with DMA in various media are summarized in Table 4. [4] The acceleration of the reaction due to dehydration of the diazonium ions was obviously shown in

Table 4. Observed rate constants of diazo-coupling reactions of *p*-methylbenzenediazonium salts with DMA in various media at 25℃



($X^- = BF_4^-$, $TFPB^-$)

	50% aq. CH_3CN[a]	wet CH_2Cl_2[b]	anhyd CH_2Cl_2[b]
k_{obs}	k_1 [DMA]	k_1 [DMA] + k_3 [DMA]^2	k_3 [DMA]^2
k_{obs}[c]	3.14×10^{-4}	1.66×10^{-2}	1.81×10^{-2}
k_{obs} ratio	1	53	58

a) *p*-methylbenzenediazonium BF_4^- was used. b) *p*-methylbenzenediazonium $TFPB^-$ was used.
c) [DMA] = 2.0×10^{-3} mol dm^{-3}.

the relative values of k_{obs} ; 1 (50% acetonitrile-50% water), 53 (wet dichloromethane), and 58 (anhydrous dichloromethane). At the same time, the change of solvent polarity resulted in the change of the kientics; k_{obs} in 50% aqueous acetonitrile was proportional to the concentration of DMA (the rate determining σ-complex formation) and in anhydrous dichloromethane proportional to the square of that of DMA (the rate-determining deprotonation), while in wet

dichloromethane both DMA and water served as base competitively in the diazo-coupling reaction.

The reaction rates of substituted benzenediazonium ions with a nucleophile under given conditions provide a typical example of the Hammett's relationship in its classical form as given in Eq. 1; k_H and k_X refer to the rate constants of the benzenediazonium ion and its *m*-or *p*-X-substituted derivatives, respectively, with a given coupling component.

$$\log k_X - \log k_H = \rho\sigma_X \qquad \text{(Eq. 1)}$$

Good linear correlations between log k_X and the substituent constant, σ_X, were obtained with respect to the rate constant (k_1) of the initial σ-complex formation step of the diazo coupling of the substituted benzenediazonium salts with DMA in various media (Table 5).

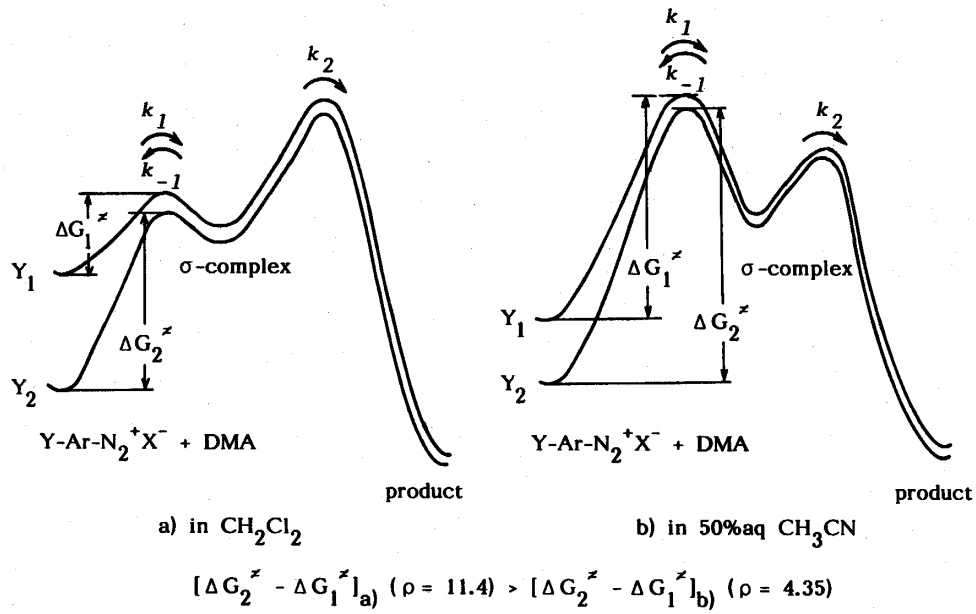
Table 5. Kinetic data of diazo-coupling reactions of substituted benzenediazonium salts with DMA under pseudofirst-order conditions.

Substituents	k_1 / s^{-1} dm^3 mol^{-1}		
	50% aq CH_3CN[a]	CH_2Cl_2[b] [c]	$CBrF_2CBrF_2$[b]
p-OCH_3	—	6.02	3.79
p-*t*-C_4H_9	—	370	36.5
p-CH_3	0.156	1.92×10^2	37.8
		($k_H / k_D = 1.74$)[d]	($k_H / k_D = 0.977$)[d]
m-CH_3	—	877	137
H	0.897	6.02×10^3	—
p-F	2.89	6.07×10^4	—
p-Br	7.92	—	—
ρ	4.35	11.4	7.80

a) Substituted benzenediazonium BF_4^- salts were used. b) Substituted benzenediazonium $TFPB^-$ salts were used. c) $[DMA]/k_{obs} = 1/k_1 + (k_{-1}/k_1 k_2)/[DMA]$. d) *N*, *N*-dimethylaniline-2, 3, 6-d_3 was used.

It is remarkable that ρ value of 11.4 obtained in dichloromethane is the highest value to the best of our knowledge of the diazo-coupling reaction.[11] As discussed above, the diazonium ions in dichloromethane are highly activated in a "naked" form, then an electron-donating effect of the substituent reflects upon the electron-demand of the cationic center of diazonium ions much more sensitively than that of the same cationic center stabilized by solvation in polar solvents. These situation are clearly reflected on the high ρ value in dichloromethane and that as low as 4.35 in 50% aqueous acetonitrile (Fig. 5).

Another interesting result in Table 5 was that the isotope effects, k_H/k_D, were 1.74 and 0.977 in dichloromethane and in DF-114B2, respectively, which means that the rate determining step changed from the deprotonation in dichloromethane to the σ-complex formation in DF-114B2. Furthermore, k_1 and ρ values of the reaction in DF-114B2 were lower than those in dichloromethane. According to the above discussion, one would expect that in less polar DF-114B2, whose dielectric constant (ε =2.34) is much smaller than that of dichloromethane (ε =

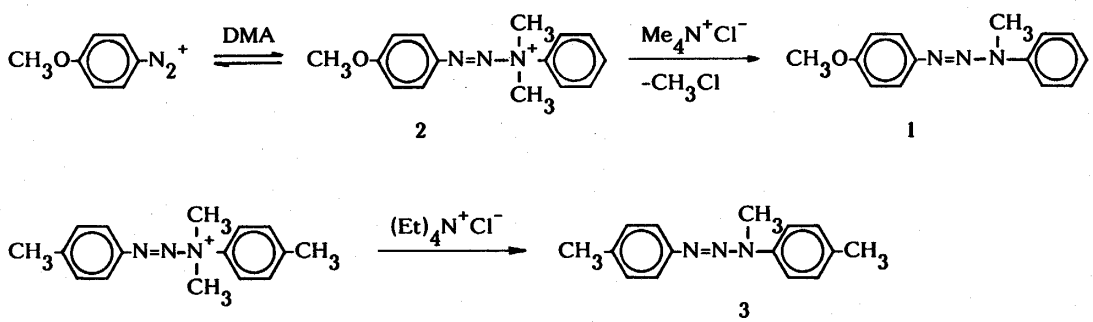


$[\Delta G_2^{\neq} - \Delta G_1^{\neq}]_{a)}$ (ρ = 11.4) > $[\Delta G_2^{\neq} - \Delta G_1^{\neq}]_{b)}$ (ρ = 4.35)

Fig. 5 Schematic reaction paths of diazo-coupling reactions in less polar dichloromethane and polar 50% aq. acetonitrile.

8.93), the diazonium ion could be highly activated to give larger k_1 and ρ values compared with those values of the reaction in dichloromethane and also the rate-determining step might be in deprotonation. The observed discrepancies seem, therefore, to suggest that another kind of mechanism might be operative in the present diazo-coupling system in a highly less polar DF-114B2. Although we need further kinetic data for detailed mechanistic investigations on the reaction in DF-114B2, we propose tentatively the following scheme to account for the above interesting observations.

Penton and Zollinger have reported the formation of diazoaminobenzene (**1**) with loss of *N*-methyl group from triazenium ion (**2**) by addition of tetramethylammonium chloride to the mixture of *p*-methoxybenzenediazonium ions and DMA in anhydrous acetonitrile (Scheme 9).[12] Similarly we could confirm the formation of diazoaminobenzene (**3**) by addition of tetraethylammonium chloride to the mixture of *p*-methylbenzenediazonium TFPB and *N,N*-dimethyl-*p*-



Scheme 9

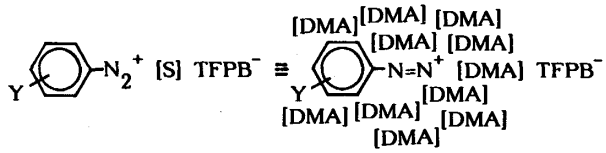
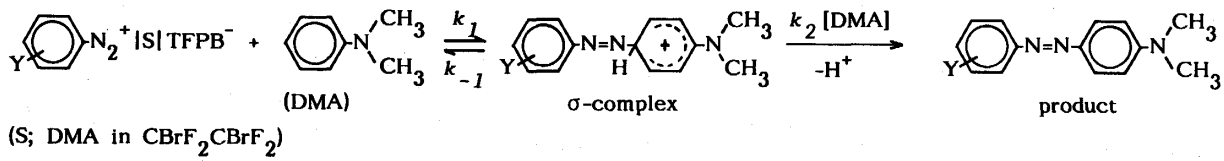


Fig. 6 Schematic representation of diazonium-DMA aggregates formed in nonpolar media.

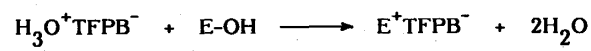
toluidine in dichloromethane and in DF−114B2. These facts imply that prior to C-coupling to give the σ-complex, the initial formation of a molecular complex by ion-dipole or Lewis acid-base type interaction between diazonium ions and amino nitrogen of DMA or *N*-coupling process exists in its extreme situation. In nonpolar solvent such as DF−114B2, which is impossible to stabilize diazonium ions by solvation, DMA might form a molecular complex or higher-order aggregates with the diazonium ions (Fig. 6), since a few hundred times molar amounts of DMA relative to the diazonium ions are added to hold the effective concentration enough for pseudo-first-order kinetic measurements (Scheme 10). This postulate of complex formation (microenvironmental solvation) provides a reasonable explanation for the lower k_1 and ρ values in DF−114B2 compared with those in dichloromethane and the rate-limiting σ-complex formation. Similar molecular complex formation has been discussed in the precise kinetic investigations on the diazo-coupling reactions of *p*-methoxybenzenediazonium ions with DMA and *m*-toluidine in anhydrous acetonitrile. [13]



Scheme 10

Some Applications of Oxonium TFPB to Anionic PTC Reactions

When sodium TFPB is added to a dichloromethane-aqueous sulfuric acid two-phase system, TFPB anion incorporates oxonium ion from the aqueous phase into the organic one quatitatively by exchanging sodium ion. As a general scheme, oxonium TFPB in the organic phase can serve to generate therein any electrophilic reagents, E^+, by proton-catalyzed dehydration from the corresponding precursors, EOH, (Scheme 11), and promote catalytically electrophilic reactions in the two-phase systems.



Scheme 11

We demonstrate here the following examples of PTC reactions catalyzed by oxonium TFPB;

i) Friedel-Crafts alkylation:

$$R\text{–}OH + Ar\text{-}H \longrightarrow Ar\text{-}R + H_2O$$

ii) Hydrolysis of ester:

$$RCOOR' + H_2O \longrightarrow RCOOH + R'\text{–}OH$$

iii) Nitrosation:

$$HNO_2 + Ar\text{-}H \longrightarrow Ar\text{-}NO + H_2O$$

Friedel-Crafts Alkylation. Oxonium ions incorporated by TFPB into the organic phase of the two-phase system is hydrated by water saturated in dichloromethane. A degree of hydration of oxonium ion in the organic phase, *i.e.*, an activity of oxonium ion in the same phase can be estimated from an equilibrium between triphenylmethyl alcohol and triphenylmethyl cation therein (Scheme 12) by defining an acidity function in the organic phase, C_{org}, according to Eqs. 2 and 3. [4]

$$\underset{(ROH)}{Ph_3COH} + H^+ \rightleftharpoons \underset{(R^+)}{Ph_3C^+} + H_2O$$

Scheme 12

$$K_{R^+} = \frac{\alpha_{ROH}\,\alpha_{H^+}}{\alpha_{R^+}\,\alpha_{H_2O}} \qquad \text{(Eq. 2)}$$

$$C_{org} = pK_{R^+} - \log([R^+]/[ROH]) \qquad \text{(Eq. 3)}$$

where the following notations are defined in the organic phase; C_{org}: acidity function, α_{ROH}: activity of triphenylmethyl alcohol, α_{H^+}: activity of oxonium ion, α_{R^+}: activity of triphenylmethyl cation, α_{H_2O}: activity of water, [ROH]: concentration of triphenylmethyl alcohol, and [R^+]: concentration of triphenylmethyl cation.

The concentration of water saturated in the dichloromethane phase in the two-phase system decreased from 1850 to 1300ppm linearly with an increased concentration of sulfuric acid in the aqueous phase from 0 to 3.5mol dm^{-3} in the presence of sodium TFPB (4.73×10^{-5}mol dm^{-3}). A rather small decrease in the concentration of water in the organic phase resulted obviously in a steep increase in the activity of oxonium ion therein as indicated by the increase in C_{org} (Table 6).

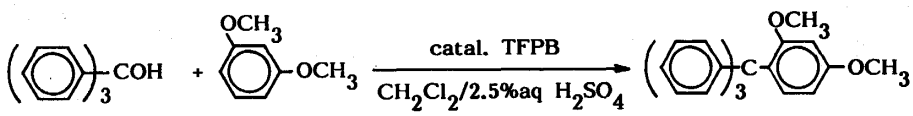
The present acidity function in the organic phase, C_{org}, gave a good correlation with the similar function, C_o, defined by Deno and Jaruzelski for the equilibrium between triphenylmethyl alcohol and triphenylmethyl cation in aqueous sulfuric acid. [14]

Table 6. Acidity function, C_{org}, of oxonium TFPB in dichloromethane

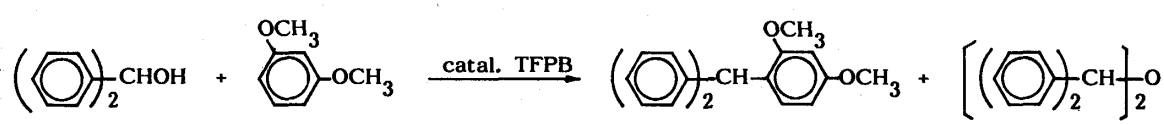
aq H_2SO_4 Concn./wt%	C_{org}[a)]
3.1	−6.13
6.6	−6.23
17.4	−6.47
25.1	−6.91
31.7	−7.37
38.8	−7.91
54.3	−8.37
59.0	−9.00

a) $C_{org} = pK_R^+ - \log([R^+]/[ROH])$, where $pK_R^+ = -6.63$ (Ph_3COH in aq H_2SO_4), $[Ph_3COH] = 1.63 \times 10^{-5}$ mol dm^{-3}, and $[NaTFPB] = 1.11 \times 10^{-4}$ mol dm^{-3}.

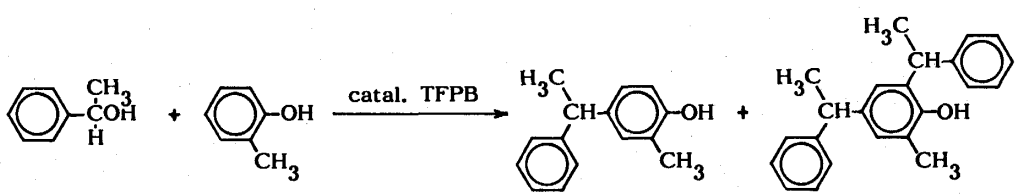
Highly activated oxonium TFPB in the dichloromethane phase could be successfully applidt o Friedel-Crafts alkylation under PTC conditions as exemplified in Scheme 13–16. Schematicre presentation of Friedel-Crafts alkylation in the PTC system is shown in Fig. 7.



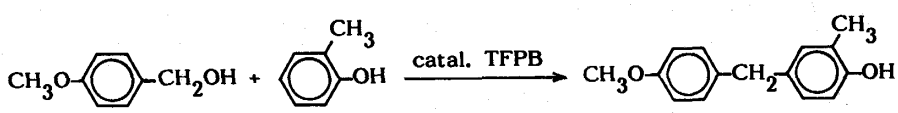
Scheme 13



Scheme 14



Scheme 15



Scheme 16

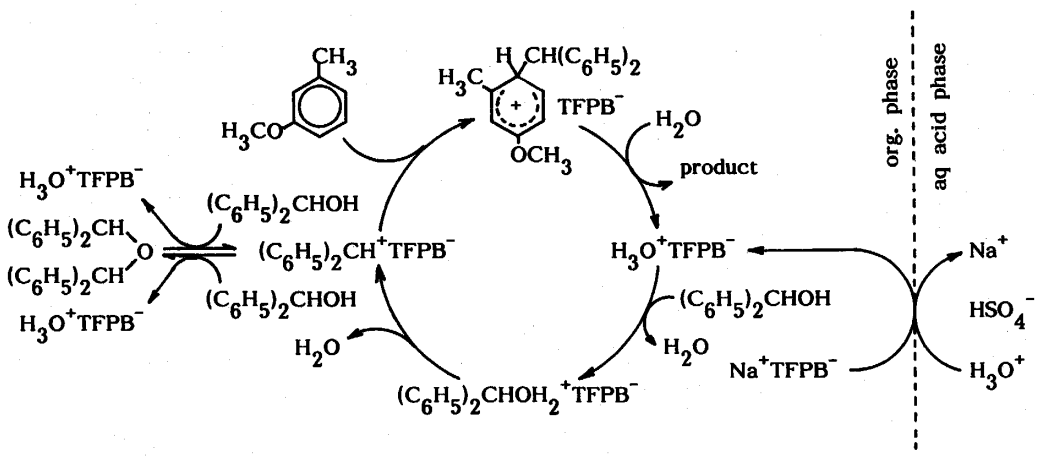
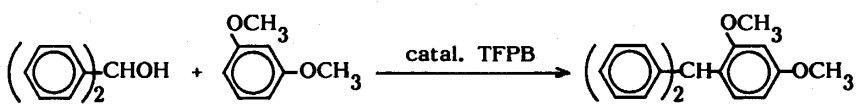


Fig. 7 Reaction scheme of phase-transfer catalyzed Friedel-Crafts alkylation.

The effect of the increase in sulfuric acid concentration on the second-order-rate constant, k_2, of diphenylmethylation of *m*-methylanisole in the two-phase system (Scheme 17) is shown in Table 7.



Scheme 17

Table 7. Effect of H_2SO_4 concn. on Friedel-Crafts alkylation in CH_2Cl_2-aq H_2SO_4 two-phase system

Rate Constants	H_2SO_4 Concn. / mol dm^{-3}		
	0.5	1.5	2.5
$k_{obs} \times 10^4$ / s^{-1}	1.31	2.57	3.81
k_2 / dm^3 mol^{-1} s^{-1}	3.97	7.79	11.4

In contrast to oxonium TFPB, other organic acids such as trifluoromethanesulfonic acid, dodecylbenzenesulfonic acid, or 3,5-di-*t*-butyl-2-hydroxybenzenesulfonic acid did not effect at all as a phase-transfer catalyst for Friedel-Crafts alkylation. Thus, oxonium TFPB in the two-phase system is at present a sole effective catalyst for Friedel-Crafts alkylation under PTC conditions.

Hydrolysis of Esters. [4] Proton-catalyzed hydrolysis of esters was performed in dichloromethane-aqueous sulfuric acid two-phase systems with TFPB catalyst. This type of PTC reaction has been once faultily reported to proceed with tetraphenylborate (TPB) in a cyclohexane-aqueous hydrochloric acid two-phase system,[15] in which actually proton-mediated decomposition

Table 8. Hydrolysis of esters in CH_2Cl_2-aq H_2SO_4 two-phase system

Esters	H_2SO_4 Concn./wt %	Reaction Time/h	Conversion %
$Ph_2CHOCOPh$	4.5	0.5	81
p-$MeOC_6H_4CH_2OCOPh$[b)]	17.5	19.5	82
p-$MeC_6H_4CH_2OCOPh$	64.5	0.3	97
p-$ClC_6H_4CH_2OCOPh$[c)]	64.5	2.3	33
$PhCH_2OCOPh$	64.5	4.0	83
t-BuOCOPh	64.5	0.1	100
PhCH(Me)OCOPh	44.1	14.0	100
$Me_2CHOCOPh$	64.5	18.5	5
MeOCOPh	80.9	2.3	5
PhOCOPh	80.9	2.3	7

a) 16-18 mol% of NaTFPB is present, unless otherwise stated. d) NaTFPB content is 0.2mol%.
c) NaTFPB content is 40.1 mol%.

of TPB occurred.[16] As shown in Table 8, TFPB was effective especially for the phase-transfer-catalyzed hydrolysis of various esters which proceed *via* $A_{AL}1$ mechanism to give stable carbocation intermediates by alkyl-oxygen bond cleavage. Similar to the above Friedel-Crafts alkylation, dodecylbenzenesulfonic acid did not effect as phase-transfer catalyst at all for the hydrolysis of ester under two-phase conditions.

Good correlation was obtained between log k_2 and the acidity function in dichloromethane, C_{org}, where k_2 denotes the second-order-rate constant of the hydrolysis of diphenylmethyl benzoate in the two-phase system (Fig. 8), which evidently indicates that the hydrolysis proceeds by $A_{AL}1$ mechanism *via* diphenylmethyl cation.

Regarding the hydrolysis of p-substituted benzyl benzoate in the two-phase system, correlations of log (k_X/k_H) with Hammett's σ and Brown-Okamoto's σ^+ values gave satisfactory

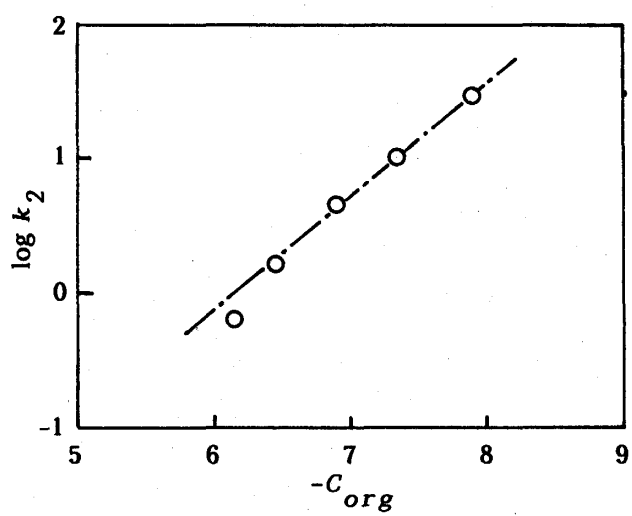


Fig. 8 Correlation between second-order rate constants of TFPB-catalyzed acid-hydrolysis of diphenylmethyl benzoate and acidity function, C_{org}.

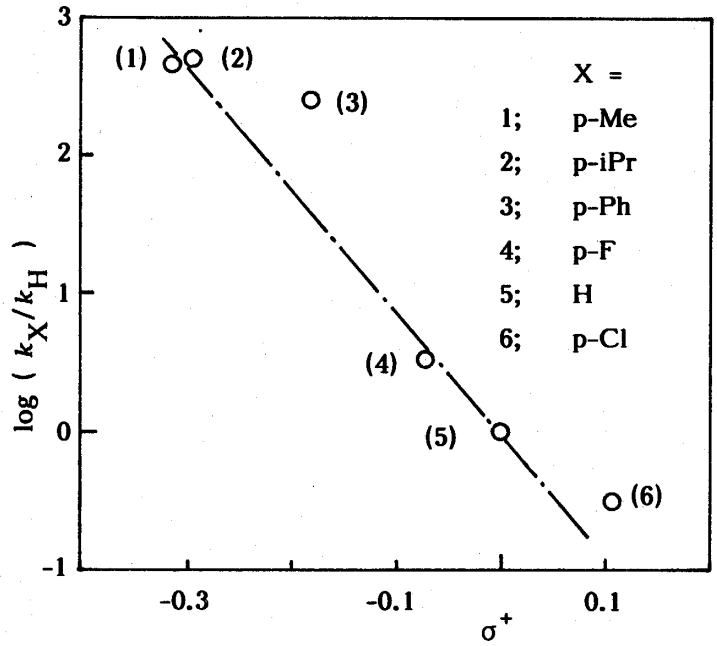


Fig. 9 Substituent effect on TFPB-catalyzed acid-hydrolysis of *p*-substituted phenyl benzoates in CH_2Cl_2-H_2SO_4 two-phase system catalyzed with TFPB.

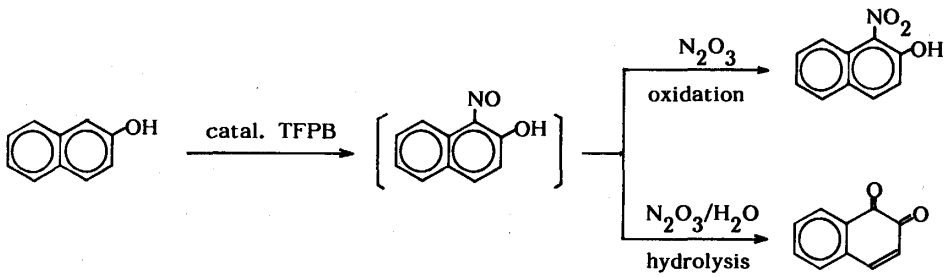
linear lines with ρ values of −9.2 and −8.6 in the two-phase systems containing 54.3 w/w% and 64.5 w/w% sulfuric acid, respectively, where k_X refers to the second-orderrate constants of the hydrolysis of the substituted benzyl benzoates with *p*-isopropyl, *p*-methyl, and *p*-flouoro substituents on the benzyl group, and k_H refers to that of benzyl banzoate (Fig. 9).

These ρ values in the two-phase systems are quite different from that of −5.7 for the acetolysis of substituted benzyl tosylate which proceeds similarly *via* benzyl cation intermediate,[17] while rather close to a limiting ρ value of −11.6 for the solvolysis of a series of substituted benzyl methanesulfonates in 97% hexafluoroisopropanol, a solvent of high ionizing power and low nucleophilicity.[18] Therefore, the present hydrolysis of benzyl esters promoted by oxonium TFPB in dichloromethane proceeds *via* an extremely dehydrated transition state, where is formed a highly electron-demanding benzyl cation intermediate.

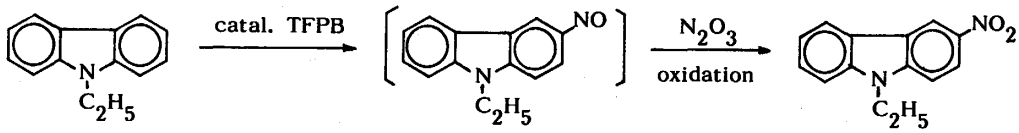
Nitrosation. Nitrosation of some aromatic compounds was examined in dichloromethane-aqueous two-phase system under TFPB-catalyzed PTC conditions as shown in Scheme 18 and 19.

Nitrosation of primary aromatic amine gave arenediazonium ions, which could be available without isolation for successive diazo-coupling reactions in the organic phase (the *in situ* diazo-coupling reaction) (Fig. 10).

Another effective application of *in situ* diazo-coupling reactions with perfluoroarenediazonium ions were already described above.



Scheme 18



Scheme 19

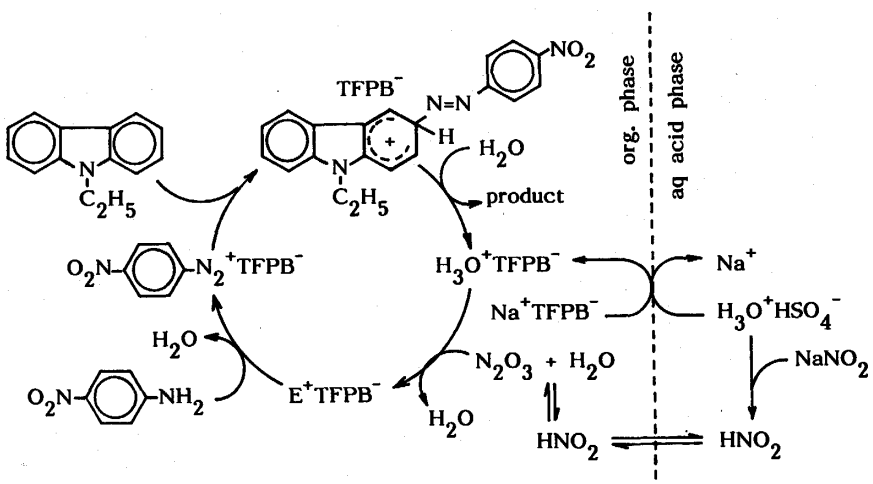
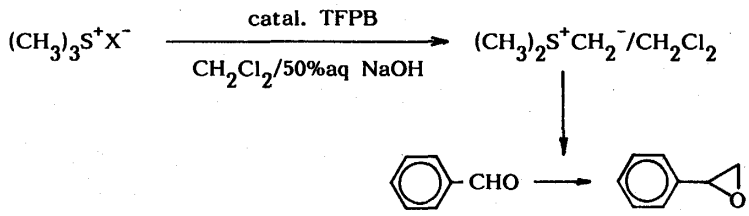


Fig. 10 Phase-transfer catalyzed nitrosation and subsequent reactions, where E^+ denotes nitrosating agent, *e.g.*, NO^+ and $HN_2O_3^+$.

Sulfonium Ylide Reactions

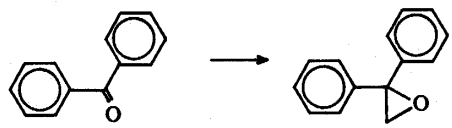
TFPB anion was used to incorporate sulfonium ion into an organic phase to generate sulfonium ylide for oxyrane formation in the dichloromethane-aqueous sodium hydroxide two-phase system (Scheme 20–23). [19]



Scheme 20

Scheme 21

Scheme 22



Scheme 23

Redox Reaction with Methylviologen TFPB as Electron Mediator across Organic Liquid Membrane

Hydrophilic methylviologen, MV^{2+}, could be incorporated into a dichloromethane phase in the form of ion pair, $MV^{2+}(TFPB^-)_2$, and its reduced form of cation radical, $MV^{+\bullet}TFPB^-$, was shown to work as an efficient catalytic electron mediator across a dichloromethane liquid membrane.[20] Thus, the associated ion pair of $MV^{2+}(TFPB^-)_2$ in dichloromethane was capable to transfer electron from a reductant of sodium dithionite in one aqueous phase to an oxidant of ferricyanide in the other aqueous phase which was separated from the former aqueous phase by a dichloromethane liquid membrane. In this case sodium-ion transport was also coupled with the electron transfer in the same direction (Fig. 11).

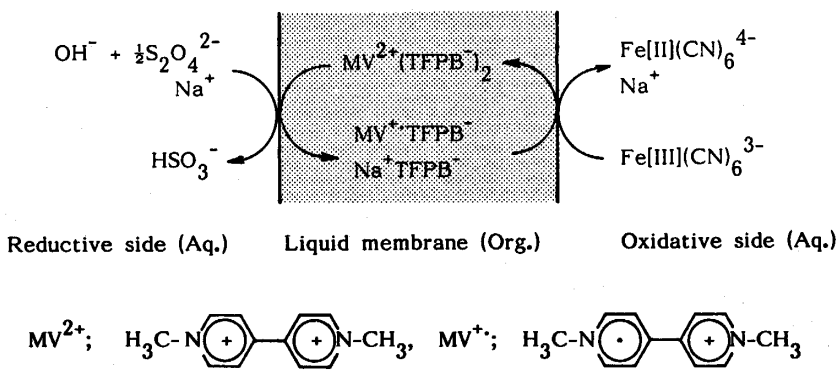


Fig. 11 Schematic representation of redox reaction in liquid-membrane system.

Future Prospects

On the bases of the results of our recent investigations, the nobel properties of trifluoromethyl-substituted tetraarylborate ions and their successful applications to various reaction systems are reviewed. Their notable specialities are excellent lipophilicity to incorporate ionic

species into hydrophobic media and high durability against acids and oxidants, and they should be ascribable to the presence of trifluoromethyl groups in the structures. The origin and nature are, however, not completely understood at present, and therefore, our efforts will be focussed hereafter to elucidate the essential structures and mechanisms of the specialities to attain much higher efficiencies, and directed to develop their applications to the photochemical functions of ionic chromogens in various hydrophobic systems.

References

1) "Phase Transfer Catalysis," ed C. M. Starks, American Chemical Society, Washington, D. C. (1987); W.E. Keller, "Phase Transfer Reactions. Fulka Compendium," Georg Thieme Verlag, Stuttgart, Vol. 1 (1986), Vol. 2 (1987); E. A. Dehmlow and S. S. Dehmlow, "Phase Transfer Catalysis," Verlag Chemie, Weinheim (1983); C. M. Starks and C. L. Liotta, "Phase Transfer Catalysis, Principles and Techniques," Academic Press, New York (1978); W. P. Weber and G.W. Gokel, "Phase Transfer Catalysis in Organic Synthesis," Springer Verlag, Berlin (1977).
2) A. R. Butler and P. T. Shephard, *J. Chem. Res. (M)*, **1978,** 4464; M. Ellwood, J. Griffiths, and P. Gregory, *J. Chem. Soc., Chem. Commun.*, **1980,** 181; D. E. Rosenberg, J. R. Beadle, S. H. Korzeniowski, and G. W. Gokel, *Tetrahedron Lett.*, **21,** 4141 (1980).
3) J. N. Cooper and R. E. Powell, *J. Am. Chem. Soc.*, **85,** 1590 (1963); G. Witting, G. Keicher, A. Ruckert, and P. Raff, *Ann.*, **563,** 110 (1949); H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83,** 2159, 2164, 2167 (1961); J. J. Eisch and R. J., Wilcsek, *J. Organomet. Chem.*, **71,** C-21 (1974); J. L. R. Williams, J. C. Doty, P. J. Grisdale, R. Searle, T. H. Regan, G.P. Happ, and D. P. Maier, *J. Am. Chem. Soc.*, **89,** 5153 (1967).
4) Unpublished data. Details will be described elswhere in near future.
5) H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **57,** 2600 (1984).
6) H. Kobayashi, T. Sonoda, and H. Iwamoto, Chem. Lett., 1981, 579; *Bull. Chem. Soc. Jpn.*, **56,** 796 (1983).
7) J. F. Bunnett and G. B. Hoey, *J. Am. Chem. Soc.*, **80,** 3142 (1958).
8) H. Iwamoto, T. Sonoda, and H. Kobayashi, *J. Fluorine Chem.*, **24,** 535 (1984).
9) G. M. Brooke, E. J. Forbes, R. D. Richardson, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, **1965,** 2088; R. E. Banks, A. R. Thompson, and H. S. Vellis, *J. Fluorine Chem.*, **22,** 499 (1983); R. D. Chembers, J. Hutchinson, and W. K. R. Musqrave, *J. Chem. Soc.*, 1965, 5040.
10) H. Iwamoto, T. Sonoda, and H. Kobayashi, *Tetrahedron Lett.*, **24,** 4703 (1983).
11) I. Szele and H. Zollinger, "Azo Coupling Reactions, Structures and Mechanisms," in "Topics in Current Chemistry," ed. F. L. Boschke, Springer Verlag, 1983, Vol.112, p.1.
12) P. N. Juri and R. A. Bartsch, *J. Org. Chem.*, **44,** 143 (1979); **45,** 2028 (1980).
13) J.R. Penton and H. Zollinger, *J. Chem. Soc., Chem. Commun.*, **1979,** 819; Helv. Chim. Acta, **64,** 1728 (1981).
14) N. C. Deno and J. J. Jaruzelski, *J. Am. Chem. Soc.*, **77,** 3044 (1955).
15) D. W. Armstrong and M. Godat, *J. Am. Chem. Soc.*, **101,** 2491 (1979).
16) S. Snips and W. Herriott, *J. Am. Chem. Soc.*, **101,** 6441 (1979).
17) A. Streitwieser, Jr., H.A. Hammond, R.H. Jagow, R.M. Williams, R.G. Jesaitis, C.J. Chang, and R. Wolf, *J. Am. Chem. Soc.*, **92,** 5141 (1970).
18) X. Creary and T. L. Underiner, *J. Org. Chem.*, **50,** 2165 (1985).
19) Y. Shiraki, N. Onitsuka, K. Takuma, T. Sonoda, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **58,** 3041 (1985).
20) K. Takuma, T. Sonoda, and H. Kobayashi, *Chem. Lett.*, **1984,** 243.