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Anion-catalyzed Phase-transfer Catalysis. I. Application to Diazo-coupling Reactions

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Anion-catalyzed phase-transfer catalysis was evidenced in the diazo-coupling reactions of the arenediazonium ion with a range of diazophile components in liquid-liquid- and liquid-solid two-phase systems. The tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ion was effective as an anionic catalyst to accelerate the reactions. Comparisons of the reaction rates in the two-phase system with those in solution systems indicated that the acceleration was due to the increased activity of the cationic reagent, partly by solubilization and partly by the dehydration of such cationic species in the nonpolar organic phase.

A great number of studies of phase-transfer catalysis (PTC) have appeared in the literature during the last decade.[1] All but a few applications thus far reported have been nucleophilic or base-mediated reactions catalyzed by an oleophilic organic cation, such as the tetraalkylammonium ion or the crown ether–metal complex. An electrophilic reaction may also proceed in a PTC manner if an appropriate anionic catalyst is provided. A few examples of this class have been verified in some reactions of the arenediazonium ion,[2] though such attempts at verification have not always been successful. This seems to have been due to the lack of an efficient anionic catalyst suitable for this purpose. In fact, very few stable organic anions have been known except for the conjugate bases of organic acids. Among them we directed our attention to the tetraphenylborate (TPB) anion as a possible anionic phase-transfer catalyst. The structural features of TPB were considered to be that the negative charge was formally localized on the central boron atom and that the hydrophilic-anion center was shielded by lipophilic phenyl ligands configured in a tetrahedrally symmetrical array.[3] Various types of homolog and their salts are conveniently discussed in the literature.

In the anion-catalyzed PTC process, the reactions were generally acid-mediated, and the leaving group upon the reaction was a proton or protonated species. In this respect, the catalyst anion had to be stable enough in an acid medium. Also, the reaction should be conducted in a nonpolar organic solvent immiscible with water in a manner like that formerly used in the traditional PTC process.

The TPB anion was, however, highly susceptible to proton-catalyzed decomposition,[4] and its solubility in nonpolar organic solvents was not always satisfactory for a phase-transfer catalyst.[5] Therefore, our efforts were focussed on improving the drawback of chemical instability[6] and, at the same time, attaining a higher solubility into the organic media by virtue of introducing a trifluoromethyl group on the phenyl rings of TPB.[7]

During the course of our studies aimed to producing the present tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) anion,[8] an application of the PTC process was reported in the acid-mediated hydrolysis of esters by the use of an ordianry TPB anion as a phase-transfer catalyst,[9] though it was shortly thereafter revealed to be false;[10] TPB is not long-lasting in such acid media.

The present paper will describe phase-transfer catalyzed diazo-coupling reactions, in which a typical onium ion acts as an electrophile, by the use of TFPB as a catalyst in two-phase systems consisting of a non-donating, inert organic phase and a solid or an aqueous one.[11] It should be noted that the present catalyst was contrived to be more oleophilic and especially durable in acid media than the parent TPB anion; sodium TFPB remained intact for more than 9 h in a vigorously stirred two-phase system of dichloromethane and 4 mol dm^{-3} sulfuric acid, and the second-order rate constants of the acid-catalyzed hydrolysis of TFPB and TPB salts in aqueous ethanol were 1.3×10^{-4} and 1.6×10^{-3} mol^{-1} dm^3 s^{-1} at 25 °C respectively. Under the present experimental conditions, therefore, the great majority of TFPB anions remain in the organic phase, and one can neglect the acid-catalyzed decomposition of TFPB by the proton which is liberated on the electrophilic aromatic substitution.

Results and Discussion

Diazo-coupling in a Liquid-solid PTC System. The dissolution of benzenediazonium tetrafluoroborate (**1**) into a benzene solution was followed by monitoring the absorbance of **1** at 300 nm. The absorbance of a supernatant containing sodium TFPB increased with the lapse of time and attained saturation within 1 h, while the dissolution rate varied with the fineness of the powdered **1**. Without the addition of sodium TFPB, we observed no indication of **1** being dissolved in the solvent; the absorbance was kept at nothing.

The suspension of the powdered **1** in a benzene solution of twice the molar amount of *N*,*N*-dimethylaniline (**2**) gave no color change, even upon vigorous agitation. The addition of a 20% molar amount of sodium TFPB to the suspension with moderate stirring at room temperature caused a rapid red-color development, where the added sodium TFPB was dissolved in the solution.[12] A 1-h reaction then afforded the coupling

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product, 4-dimethylaminoazobenzene (**3**), in an 86% yield. In a similar manner, twice the molar amount of phenol (**4**) gave 4-hydroxyazobenzene (**5**) in a quantitative yield after a 3-h reaction in the presence of twice the molar amount of 2,6-dimethylpyridine (**6**). No diazo-coupling with phenol in the organic phase proceeded without the addition of a base such as **6**.[13]

The acceleration of the diazo-coupling rate can be attributed predominantly to the dissolution of the arenediazonium ion into the solvent by ion-pairing with the TFPB anion. The coupling reactions in the absence of the TFPB anion were negligible, though possibly taking place on the surface of the solid diazonium salt (**1**).

Diazo-coupling in a Liquid-liquid PTC System. In a two-phase system consisting of an aqueous 4-nitrobenzenediazonium tetrafluoroborate (**7**) and a dichloromethane solution of an equimolar amount of 9-ethylcarbazole (**8**), the vigorous agitation of the two-phase mixture resulted in a faint red coloration after a while, but no more color was developed by further, prolonged agitation. The addition of one-fifteenth the molar amount of sodium TFPB to the mixture immediately turned it dark red. The two-phase system formed no emulsion and was separated into two layers as soon as agitation stopped. After 3 h of continuous, vigorous stirring, the diazonium test by *N,N*-dimethylaniline was negative to the aqueous phase, and then the coupling product was isolated in an 80% yield. In a similar manner, the reactions of **7** with two kinds of diphenylamines, **9** and **10**, and three kinds of anisole derivatives, **11**, **12**, and **13**, gave the corresponding coupling products. The results are summarized in Table 1. A comparison of the latter three examples seemed to suggest a rather large substituent effect of diazophile components upon the reaction rate and yield. It is worthwhile noting that the coupling of **7** with **8** was found to afford the coupling product in a yield of less than a 2% after a 5-h reaction when the reaction was carried out in aqueous acetic acid.[14] From the comparisons of the yield and the reaction period, one can readily notice the efficiency of the present PTC system.

Diazotization and diazo-coupling could be conducted successively in one pot without any isolation of diazonium salt. The process was exemplified by PTC, consisting of a dichloromethane solution of **8** and an aqueous solution of 4-nitrobenzenediazonium salt, in the presence of a 1% molar amount of sodium TFPB. The conversion attained up to 94%, based upon the amount of sodium nitrite added after the 5-h reaction at room temperature. This procedure can provide a convenient method of diazo-coupling in general; it might be especially useful in reactions with the diazonium salts, which are too labile to be isolated.

Table 1. Phase-transfer catalyzed diazo-coupling in an aqueous-CH_2Cl_2 two-phase system[a)]

Diazophile	Reaction time	Yield[b)]
	h	%
9-Ethylcarbazole (**8**)	3	80
Diphenylamine (**9**)	2	76
N-Methyldiphenylamine (**10**)	3	85
Anisole (**11**)	48	10[c),d)]
m-Methylanisole (**12**)	12	50[d)]
m-Methoxyanisole (**13**)	2	85[e)]

a) The reaction was carried out at room temperature. b) Yield of the isolated product. c) A 10-fold molar excess of the diazophile was added. d) The aqueous phase was buffered at pH 7. e) The aqueous phase was not buffered, and the aqueous phase was found to be acid after the reaction.

Diazo-coupling in Homogeneous Phases. Kinetics and Mechanism. In connection with the diazo-coupling in liquid-liquid two-phase systems, the reaction rates were examined in homogeneous solution phases of aqueous and non-donating inert organic solvents separately. A solution of arenediazonium TFPB in such an organic solvent was prepared by ion exchange between the corresponding arenediazonium tetrafluoroborate in the solid state and sodium TFPB dissolved in the organic solvent to be examined. The kinetics of the diazo-coupling reaction of *N,N*-dimethylaniline (**2**) with benzenediazonium salt was followed under the pseudo-first-order conditions in the latter. A general expression of the reaction rate was given by Eq. 1, with the assumption that no exchange of the diazonium ion occurred between the ion pair of BF_4^- and that of $TFPB^-$ in the solution phase;

$$\mathrm{d[Product]}_t/\mathrm{d}t = k_1'[\mathrm{ArN_2^+\cdot TFPB^-}] + k_1''[\mathrm{ArN_2^+\cdot BF_4^-}], \qquad (1)$$

where k_1' and k_1'' were the conditional rate constants concerning the respective diazonium salts. The ratio of $[\mathrm{ArN_2^+\cdot BF_4^-}]_{t=0}/[\mathrm{ArN_2^+\cdot TFPB^-}]_{t=0}$ in chloroform, for example, was estimated, from the ratio of $[\mathrm{Product}]_{t=\infty}$ in the absence of the TFPB anion to that in the presence of the same anion, to be about 5%.

In the absence of TFPB salt, the first term was zero, irrespective of the reaction medium; then, assuming $[\mathrm{Product}]_{t=0}=0$, we obtained:

$$\ln([\mathrm{Product}]_{t=\infty}) - \ln([\mathrm{Product}]_{t=\infty} - [\mathrm{Product}]_t) = k_1''t. \qquad (2)$$

Excellent pseudo-first-order kinetic plots were obtained according to Eq. 2 with a correlation coefficient (γ) greater than 0.99 in each system of the tetrafluoroborate with **2** as well as **4**.

An examination of the rate constants indicated that the reactions in dry organic solvents were second-order in **2**, while in aqueous buffers it was first-order also in **2**. These kinetic orders, in accordance with Bartsch's observation,[15] indicate that, in the dry organic phase, the reaction rate is determined by the stage of deprotonation from a σ-complex, and that the reaction requires an equimolar amount of the proton-accepting base, as is observed in the diazo-coupling of phenol in a solid-liquid PTC system. In the aqueous phase, the formation of the σ-complex would be the rate-determining step, and the subsequent deprotonation would proceed rapidly, promoted by a large excess of the water base. When the reaction was conducted in a wet chloroform which had been saturated in advance with an aqueous buffer such as would occur in an actual liquid-liquid PTC

TABLE 2. RATE CONSTANTS OF THE DIAZO-COUPLING OF *N,N*-DIMETHYLANILINE WITH BENZENEDIAZONIUM TETRAFLUOROBORATE (**1**) AND -TFPB (**11**) IN AQUEOUS AND ORGANIC SOLVENTS AT 25 °C

Solvent	Third-order rate constant, k_3/mol^{-2} dm^6 s^{-1}		Second-order rate constant, k_2/mol^{-1} dm^3 s^{-1}
	1	**11**	**1**
Benzene	c)	7.1×10^4	—
Chloroform			
anhydrous	2.9×10^4	4.6×10^5	—
wet[a)]	1.02×10^3	—	1.6
Aqueous buffer[b)]	—	—	1.7×10^{-1}

a) Saturated with the aqueous buffer at 25 °C (*ca.* 6×10^{-2} mol dm^{-3} of water). b) pH 7.02. c) Not measurable due to the low solubility of **1**.

system, the kinetic behavior was again first-order in benzenediazonium salt, while the overall reaction order in **2** was not a simple one. Instead, the kinetic data were consistent with the rate expression of a sum of two terms, one being first-order, and the other, second-order, in **2**. The two terms conceivably correspond to the respective deprotonating paths simultaneously taking place in the solution, the former, to that by the water base present in the wet organic phase, and the latter, to that by **2** itself. The rate constants thus obtained are summarized in Table 2.

Comparisons of the rate constants concerning the fluoroborate (**1**) indicate that the k_3 in wet chloroform was reduced to 1/30 of that in the dry solvent, while the k_2 in the aqueous buffer was lowered to 1/15 of that in the wet chloroform, despite the increase in the water base in the former; the reduced reactivity can be ascribed to the stabilization of the cationic reagent due to hydration in such wet media.

It can also be seen that the presence of TFPB in a benzene solution caused a distinct difference in the reaction rate, since practically no arenediazonium ion was transferred into the organic phase without the TFPB catalyst. Also, a comparison of k_3 values of **1** and **11** in dry chloroform solutions indicates that the coupling reaction with the diazonium ion paired with TFPB proceeded about sixteen times faster. Comparisons of the k_1' and k_1'' values in the reactions with phenol of an equal concentration reveal a parallel tendency, with the rate three times faster. If the ratio of $[\mathrm{ArN_2^+\cdot BF_4^-}]_{t=0}/[\mathrm{ArN_2^+\cdot TFPB^-}]_{t=0}$ is taken into account, the contribution due to the second term in Eq. 1 can be neglected in practice. The observed acceleration caused by TFPB is presumably to be ascribed to the larger size of the counter anion upon ion pairing in nonpolar organic solvents.[16)]

Kinetics and Mechanism of PTC. The kinetics in the solution phases suggested that the reaction scheme of the present PTC cycle was as is illustrated in Fig. 1. At the beginning of the reaction, the diazonium ion was exchanged for the sodium ion of the catalyst at the interface, solubilized into the organic phase, and coupled with the diazophile dissolved therein, to give a product of azo dye;

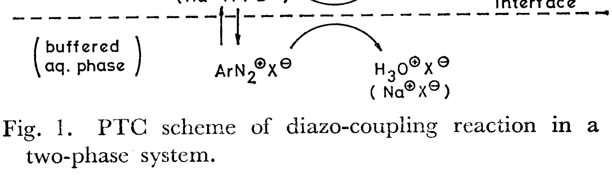

Fig. 1. PTC scheme of diazo-coupling reaction in a two-phase system.

$$(\mathrm{Na^+\cdot TFPB^-})_{\mathrm{org}} + (\mathrm{ArN_2^+})_{\mathrm{aq}} \overset{K_1}{\rightleftharpoons} (\mathrm{ArN_2^+\cdot TFPB^-})_{\mathrm{org}} + (\mathrm{Na^+})_{\mathrm{aq}}, \tag{3}$$

where

$$K_1 = [\mathrm{ArN_2^+\cdot TFPB^-}]_{\mathrm{org}}[\mathrm{Na^+}]_{\mathrm{aq}}/[\mathrm{Na^+\cdot TFPB^-}]_{\mathrm{org}}[\mathrm{ArN_2^+}]_{\mathrm{aq}} \tag{4}$$

and

$$[\mathrm{ArN_2^+\cdot TFPB^-}]_{\mathrm{org}} + [\mathrm{Diazophile}]_{\mathrm{org}} \xrightarrow{k_2} [\mathrm{Product}]_{\mathrm{org}} + [\mathrm{H_3O^+\cdot TFPB^-}]_{\mathrm{org}}, \tag{5}$$

where we assumed a slow coupling reaction relative to the mass-transfer between the two phases under an efficient stirring; the rate expression was then given by Eq. 6:

$$\mathrm{d}[\mathrm{Product}]_{\mathrm{org}}/\mathrm{d}t = k_2[\mathrm{ArN_2^+\cdot TFPB^-}]_{\mathrm{org}}[\mathrm{Diazophile}]_{\mathrm{org}}. \tag{6}$$

The liberated proton, which was in the form of an oxonium ion or some other protonated species, formed an ion pair with the TFPB anion to be transported to the interface; the proton was thrown out of the organic phase in exchange for the diazonium ion, which was used in the next PTC cycle:

$$[\mathrm{H_3O^+\cdot TFPB^-}]_{\mathrm{org}} + [\mathrm{ArN_2^+}]_{\mathrm{aq}} \overset{K_2}{\rightleftharpoons} [\mathrm{ArN_2^+\cdot TFPB^-}]_{\mathrm{org}} + [\mathrm{H_3O^+}]_{\mathrm{aq}}, \tag{7}$$

where

$$K_2 = [\mathrm{ArN_2^+\cdot TFPB^-}]_{\mathrm{org}}[\mathrm{H_3O^+}]_{\mathrm{aq}}/[\mathrm{H_3O^+\cdot TFPB^-}]_{\mathrm{org}}[\mathrm{ArN_2^+}]_{\mathrm{aq}}. \tag{8}$$

Provided the thermodynamic activities of the sodium and diazonium ions were maintained constant throughout the reaction period in an aqueous buffer, then the ratios of $[\mathrm{Na^+}]_{\mathrm{aq}}/[\mathrm{ArN_2^+}]_{\mathrm{aq}}$ and $[\mathrm{H_3O^+}]_{\mathrm{aq}}/[\mathrm{ArN_2^+}]_{\mathrm{aq}}$ were constant; they are represented by the symbols of Φ_1 and Φ_2 respectively.

Since the initial concentration of TFPB, Q_0, was given by Eq. 9, the concentration of the diazonium ion in the organic phase, $[\mathrm{ArN_2^+\cdot TFPB^-}]_{\mathrm{org}}$, was derived to be constant, as is given in Eq. 10, by combining Eqs. 4, 8, and 9:

$$Q_0 = [\mathrm{Na^+ \cdot TFPB^-}]_{\mathrm{org}} + [\mathrm{ArN_2^+ \cdot TFPB^-}]_{\mathrm{org}} + [\mathrm{H_3O^+ \cdot TFPB^-}]_{\mathrm{org}}, \quad (9)$$

$$[\mathrm{ArN_2^+ \cdot TFPB^-}]_{\mathrm{org}} = Q_0/(\Phi_1/K_1+\Phi_2/K_2+1). \quad (10)$$

In other words, the diazonium ion in the organic phase was supplied from the aqueous phase so fast, relative to the consumption rate by the reaction, that the concentration of the ion pair of $\mathrm{ArN_2^+ \cdot TFPB^-}$ in the organic phase could be maintained at a steady level. Consequently, the reaction became apparently first-order only in the diazophile in the organic phase, as is expressed in Eq. 11:

$$\mathrm{d}[\mathrm{Product}]_{\mathrm{org}}/\mathrm{d}t = k_{\mathrm{app}}[\mathrm{Diazophile}]_{\mathrm{org}}, \quad (11)$$

where;

$$k_{\mathrm{app}} = k_2Q_0/(\Phi_1/K_1+\Phi_2/K_2+1) = k_2'Q_0. \quad (12)$$

Equation 12 indicated that the apparent first-order rate constant, k_{app}, was linearly proportional to the catalyst concentration, Q_0.

Since the total moles of diazophile and product was always equal to the initial moles of diazophile, the rate equation was then given by Eq. 13 or by Eq. 14 of an integrated form:

$$\mathrm{d}[\mathrm{Product}]_{\mathrm{org}}/\mathrm{d}t = k_{\mathrm{app}}([\mathrm{Diazophile}]_{\mathrm{org},0} - [\mathrm{Product}]_{\mathrm{org}}), \quad (13)$$

$$\ln([\mathrm{Diazophile}]_{\mathrm{org},0}/([\mathrm{Diazophile}]_{\mathrm{org},0} - [\mathrm{Product}]_{\mathrm{org}})) = k_{\mathrm{app}}t. \quad (14)$$

The resulting formulations in the present process are quite analogous to those derived by Starks for the traditional cation-catalyzed PTC process.[17] The only essential difference is that each ionic species has a sign of charge which is opposite to that of the corresponding one in the traditional process.

Conditions such as those which Eqs. 11 and 13 were premised on could be accomplished in the diazo-coupling of 9-ethylcarbazole (**8**) in dichloromethane with a ten-fold excess of 4-nitrobenzenediazonium tetrafluoroborate (**7**) in an aqueous buffer in the presence of sodium TFPB if the reaction mixture was stirred at a speed such that the stirring was no longer rate-limiting.

The effect of stirring in the two-phase system is shown in Fig. 2. The initial rates were compared at various stirring speeds in the reaction of **8** with **1** in dichloromethane under an apparently first-order condition in **8**. The results indicated that, at a stirring speed higher than 400 min⁻¹, the reaction was no longer of an interfacial phenomena.

The kinetics of the formation of the azo dye from **7** and **8** was followed by monitoring the absorbance at 430 nm at 25.0 °C. Apparent first-order kinetic plots, mostly covering more than one half-life of the diazophile, were obtained with a correlation coefficient (γ) greater than 0.99, as is summarized in Table 3. The apparent rate constants thus obtained were linearly proportional to the catalyst concentration with a γ value of 0.998 in its range from 5.15×10^{-5} to 2.00×10^{-4} mol dm^{-3}, consistent with Eq. 12; the gradient of the correlation line gave the overall k_2' value of 8.9 mol^{-1} dm^3 s^{-1} in the present PTC system.

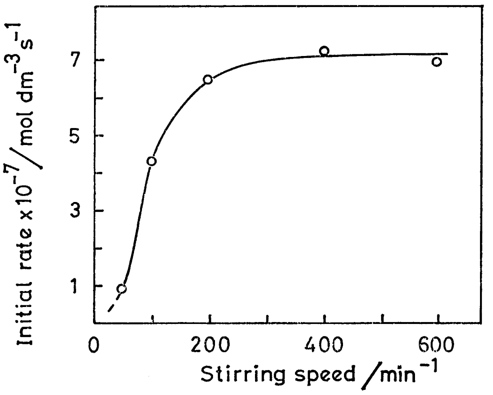

Fig. 2. Dependence of the initial reaction rate upon the stirring speed in the two-phase system.

The kinetics of the present model reactions in the two-phase system, though the diazophile and diazonium components examined fell within a rather limited range, indicated the catalyst turnover in the course of the PTC cycle and a remarkable acceleration of the *C*-coupling rate in non-donating organic solvents, irrespective of the reactivity of the diazophile component. Recently Griffiths and his co-workers reported on diazo-coupling in the PTC manner by the use of dodecylbenzenesulfonate (DBS) in a dichloromethane-aqueous buffer two-phase system.[2b] The DBS in their system, however, seems not always efficient as a phase-transfer catalyst; *e.g.*, PTC using DBS took 48 h to obtain a 44% yield from **8** and 4-nitrobenzenediazonium chloride, showing a great difference from the result of the present one-pot operation. A lower catalytic efficiency of DBS is consistent with the steric effect of an uncrowded anionic center of the sulfonate, which would favor the formation of a tight ion pair in nonpolar organic solvents and would consequently, decrease the reactivity of the counter cation. Also, they mentioned that, upon the diazo-coupling with arylamines in an anion-catalyzed PTC manner, the nucleophilicity of the amino nitrogen might affect the reaction site so as to cause *N*-coupling prior to *C*-coupling. However, such reaction behavior was unlikely so far as we have examined the present system; instead, *N*-coupling was seemingly observed only in

TABLE 3. APPARENT FIRST-ORDER RATE CONSTANTS, k_{app}, IN THE DIAZO-COUPLING OF 4-NITROBENZENEDIAZONIUM SALT WITH 9-ETHYLCARBAZOLE IN THE TWO-PHASE SYSTEM

$[\mathrm{TFPB^-}]/10^{-5}$ mol dm^{-3}	5.15	7.7	10.0	15.0	20.0
Observed range of conversion/%	41	54	57	72	85
$k_{\mathrm{app}}/10^{-4}$ s^{-1}	4.3	7.2	9.5	13.3	17.9
γ	0.992	0.996	0.996	0.998	0.995

cases of the absence of an effective proton-accepting base.

Experimental

Diazo-coupling in Liquid-solid PTC Systems. Into a stirred suspension of powdered benzenediazonium tetrafluoroborate (**1**)[18] (50 mg, 0.26 mmol) in benzene (10 ml) we added *N,N*-dimethylaniline (**2**) (66 mg, 0.55 mmol). The mixture was then colored pale yellow, but prolonged stirring caused no further reaction and gave no coupling product. Into a stirred mixture of the same compositions we added sodium TFPB (48 mg, 0.05 mmol). The mixture immediately turned red. We then kept stirring it at room temperature for 1 h. The resulting benzene layer was evaporated to dryness. The residual red solid was chromatographed on a silica-gel column; the fraction eluted with hexane gave yellow, crystalline 4-dimethylaminoazobenzene (49 mg, 86% yield) melting at 118 °C.[19]

The reaction with phenol was conducted in a similar manner except that an equimolar amount of 2,6-dimethylpyridine was added as a proton-accepting base. 4-Hydroxyazobenzene was obtained from a chromatographic fraction eluted with dichloromethane on a silica-gel column. Mp 154 °C.[20] The yield was quantitative when a double molar amount of phenol was used.

Diazo-coupling in Liquid-liquid PTC Systems. A mixture of an aqueous solution (25 ml) of 4-nitrobenzenediazonium tetrafluoroborate (**7**)[21] (70 mg, 0.3 mmol) and a dichloromethane solution (25 ml) of 9-ethylcarbazole (**8**) (55 mg, 0.3 mmol) and sodium TFPB (20 mg, 0.02 mmol) were agitated by means of a screw propeller rotating at 700 min^{-1}[22] for 3 h at room temperature; the aqueous layer was then negative to a diazonium test by *N,N*-dimethylaniline. The organic layer was evaporated to dryness. 9-Ethyl-3-(4-nitrophenylazo)carbazole (80 mg) was isolated from a chromatographic fraction eluted with dichloromethane on a silica-gel column. Recrystallization from methanol–dichloromethane gave red needles melting at 180—182 °C.[14] Found: C, 69.53; H, 4.72; N, 16.15%; *m/e*, 344 (M$^+$). The yield is tabulated in Table 1, together with those of the following reactions.

The reactions with diphenylamine (**9**) and *N*-methyldiphenylamine (**10**) were conducted in a similar manner to give 4-(4-nitrophenylazo)diphenylamine[23] of dark red needles melting at 160 °C[23] from methanol–dichloromethane (Found: C, 67.65; H, 4.15; N, 17.50%; *m/e*, 318 (M$^+$)) and 4-(4-nitrophenylazo)-*N*-methyldiphenylamine[24] of red needles melting at 174—175 °C from methanol-dichloromethane. Found: C, 68.46; H, 5.00; N, 16.79%; *m/e*, 332 (M$^+$). Calcd for $C_{19}H_{16}N_4O_2$: C, 68.66; H, 4.85; N, 16.86%; M, 332. UV$_{max}$ (CH_2Cl_2) 474 nm (ε 31900); ^{13}C-NMR ($CDCl_3$) δ=114.29, 122.77, 124.68, 125.61, 125.93, 126.22, 129.93, 144.99, 147.10, 147.62, 152.63, and 156.61; ^{1}H-NMR ($CDCl_3$) δ=3.40 (3H, s, =N–CH_3), 6.78 (2H of =N–C_6H_4–N_2–, d, J=5 Hz), 7.27 (5H, m, =N–C_6H_5), 7.77 (2H of =N–C_6H_4–N_2–, d, J=5 Hz), 7.80 (2H of –N_2–C_6H_4–NO_2, d, J=4.5 Hz), and 8.22 (2H of –N_2–C_6H_4–NO_2, d, J=4.5 Hz). The ^{1}H- and ^{13}C-NMR spectra were compatible with the assigned structure.

The reactions with anisoles were conducted in a mixture of 10 ml of a dichloromethane solution and 10 ml of an aqueous solution buffered with disodium hydrogenphosphate and potassium dihydrogenphosphate (2.0×10^{-3} mol dm^{-3} each) at pH 7.02. Each product was obtained from a chromatographic fraction eluted with dichloromethane on a silica-gel column. 4-(4-Nitrophenylazo)anisole; yellow crystallites melting at 140 °C.[25] MS: *m/e*, 257 (M$^+$). 4-(4-Nitrophenylazo)-3-methylanisole; red fibriles melting at 138 °C.[26] MS: *m/e*, 271 (M$^+$). 4-(4-Nitrophenylazo)-3-methoxyanisole; red fibriles melting at 155 °C.[27] Found: C, 58.28; H, 4.66; N, 14.56%; *m/e*, 287 (M$^+$).

Diazo-coupling in Liquid-liquid PTC System by One-pot Operation. The aqueous solution of diazonium salt was prepared by the addition of an aqueous sodium nitrite (0.170 g, 2.47 mmol, in 2 ml of water) to a solution of 4-nitroaniline (0.386 g, 2.80 mmol) in 2 mol dm^{-3} hydrochloric acid (7 ml) at 0 °C. After 1.5-h stirring, a nitrous acid test by the use of potassium iodide and starch was negative. The diazonium salt solution was stirred vigorously, together with a dichloromethane solution (20 ml) of 9-ethylcarbazole (**8**) (0.501 g, 2.57 mmol) and sodium TFPB (20 mg, 2.15×10^{-2} mmol). The absorbance of the azo dye was monitored at 430 nm. After a 5-h reaction, a diazonium test using *N,N*-dimethylaniline was negative to the aqueous phase, and the absorbance attained a plateau. The yield of azo dye was estimated by the absorbance to be 94%, based upon the amount of sodium nitrite added.

Kinetics in Solution Phases. A suspension of the diazonium salt (**1**) (10 mg, 0.05 mmol) in benzene or chloroform (50 ml) was shaken for 1 h at 25 °C with or without the addition of sodium TFPB (5 mg), the amount of which had previously been confirmed to be enough for the saturation in benzene,[12] while it dissolved completely in chloroform. The residual solid was filtered off if present. The benzene filtrate or chloroform solution was diluted with the same solvent to 10 times the original volume when TFPB was added. No dilution was needed in the absence of TFPB. An aliquot (2.00 ml) was placed in a septum-capped 10-mm photometric cell previously maintained at 25.0 °C. The absorbance was monitored immediately after the addition of a diazophile solution (1.00 ml) into the cell through the septum by means of a syringe.

The key bands for the determination of azo dyes in benzene and chloroform solutions were as follows: λ_{max} and (ε) for 4-dimethylaminoazobenzene, 410 nm (28000) and 410 nm (26000) respectively, and those for 4-hydroxyazobenzene, 345 nm (24000) and 345 nm (20000), respectively. The former azobenzene showed an ε value of 19000 at λ_{max} of 410 nm in a methanol–water (6:4 in volume) mixture; this value was used for the kinetic determinations of the azo dye in an aqueous solution buffered at pH 7.02. The resulting azo dye was less soluble in the aqueous solution, and the absorbance was followed until the reaction mixture became cloudy.

The kinetic dependence upon the concentration of *N,N*-dimethylaniline was examined in benzene, chloroform, and aqueous solutions, where the concentration ranges examined were 2.12—5.30×10^{-4}, 8—40×10^{-4}, and 1.0—5.0×10^{-3} mol dm^{-3} respectively; otherwise, the concentration was 3.80×10^{-4} mol dm^{-3}. Phenol (3.80×10^{-4} mol dm^{-3}) as a diazophile was added, together with an equimolar amount of 2,6-dimethylpyridine as a proton-accepting base. Plottings according to Eqs. 1 and 2 afforded k_1' value of 8.7×10^{-3} s^{-1} (γ=0.998) and k_1'' value of 2.7×10^{-3} s^{-1} (γ=0.991).

Kinetics in Liquid-liquid PTC Systems. An aqueous solution (25 ml) of 4-nitrobenzenediazonium tetrafluoroborate (**7**) (12 mg, 2.0×10^{-3} mol dm^{-3}), buffered with disodium hydrogenphosphate and potassium dihydrogenphosphate (2.0×10^{-3} mol dm^{-3} each) at pH 7.02 and a dichloromethane solution (25 ml) of 9-ethylcarbazole (**8**) (2.05×10^{-4} mol dm^{-3}) and sodium TFPB (5.15—20.0×10^{-5} mol dm^{-3}), both previously maintained at 25.0 °C, were put together all at once and stirred by means of a screw propeller rotating at 700 $\mathrm{min^{-1}}$. Every 2.0 min stirring was stopped, and a 100-μl portion was taken out of the dichloromethane layer. The aliquot was poured into the same solvent (3.0 ml), previously placed in a photometric cell, to determine the absorbance at 430 nm. The production of azo dye was plotted against the time lapse according to Eq. 14 to give the k_{app} for systems of different TFPB concentrations. The results are summarized in Table 3.

The plotting of k_{app} against the concentration of sodium TFPB gave a linear relationship with a γ value of 0.998, the gradient of the correlation line being 8.93 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$.

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