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TETRAKIS[3,5-DI(*F*-METHYL)PHENYL]BORATE AS THE FIRST EFFICIENT NEGATIVELY CHARGED PHASE TRANSFER CATALYST. KINETIC EVIDENCES

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Remarkable accerelation was observed by use of sodium tetrakis[3,5-di(*F*-methyl)phenyl]borate as a negatively charged phase transfer catalyst for diazonium ion in the azo coupling reactions of aryldiazonium tetrafluoroborate with a range of diazophile components in liquid-liquid- and liquid-solid two-phase systems. Kinetics of the reactions was examined to confirm the phase transfer catalysis.

Our interest in the recent progress of phase transfer catalysis (PTC) techniques[1)] by use of cationic catalyst urged us to examine negatively charged phase transfer catalysts and their application to organic reactions involving cationic reagents or intermediates in organic media of lower polarity. Very few stable organic anions have been known except the conjugate bases of organic acids. Among them we focussed our attention to tetraarylborate anions, because various types of homologues and their salts could be referred in literatures.

Taking azo coupling as a model reaction involving a cationic reagent, we have probed PTC of tetrakis[3,5-di(*F*-methyl)phenyl]borate anion (TFPB)[2)] for diazonium ion. It should be noted that the present catalyst is contrived to be more oleophilic and more durable in acid media than the parent tetraphenylborate anion (TPB); the second-order rate constants of the acid-catalyzed hydrolysis of TFPB and TPB salts in aqueous ethanol are 1.3×10^{-4} and 1.6×10^{-3} $\mathrm{mol^{-1}.l.sec^{-1}}$ at 25°C, respectively. Under the present experimental conditions, one might neglect the acid-catalyzed decomposition of TFPB by the proton which would be liberated on the electrophilic aromatic substitution.

Phenyldiazonium tetrafluoroborate (<u>1</u>) is practically insoluble in benzene. Suspension of the solid <u>1</u> in a benzene solution of *N*,*N*-dimethylaniline (<u>2</u>) (2 eq.) gave no color change even by vigorous agitation. The addition of sodium TFPB (<u>3</u>) (1/5 eq.) to the system with moderate stirring at room temperature caused rapidly red-color development, where <u>3</u> was dissolved in the solution. After 1-h reaction, the coupling product, 4-*N*,*N*-dimethylaminoazobenzene, was isolated by column chromatography on silica gel in a 86 % yield. In a similar reaction system, phenol (<u>4</u>) as a diazophile (2 eq.) gave the coupling product, 4-hydroxyazobenzene, in a quantitative yield after 3-h reaction in the presence of 2,6-lutidine of the equal moles to 4.

In another type of two-phase system consisting of aqueous 4-nitrophenyldiazonium tetrafluoroborate (5) and a dichloromethane solution of *N*-ethylcarbazole (6) (1 eq.), vigorous agitation of the mixture resulted in faint red coloration after a while, but no more color was developed by further prolonged agitation. The addition of 3 (1/15 eq.) to the mixture caused immediately dark red coloration. The two-phase system formed no emulsion and was separated into two layers as soon as agitation stopped. After 3 h with continuously vigorous stirring, the diazonium test using 2 was negative to the aqueous phase, and then the coupling product was isolated by column chromatography on silica gel in a 80 % yield.3) In a similar manner, the 2-h reactions with *N,N*-diphenylamine and *N*-methyl-*N,N*-diphenylamine gave the corresponding coupling products in 76 and 85 % yields, respectively.

If the azo coupling proceeds in a PTC manner in the present system, it should be derived that the apparent first-order rate constant (k_1) is directly proportional to the concentration of phase transfer catalyst in the organic phase under conditions that thermodynamic activities of sodium-, diazonium-, and tetrafluoroborate ions in an aqueous buffer are maintained constant and the mixture is well stirred.4) Such conditions could be accomplished in the azo coupling of 6 (5.13×10^{-6} mol) in dichloromethane (25 ml) with 5 (0.05 mmol) in 0.004 $\mathrm{mol.l^{-1}}$ aqueous buffer (pH 7.02, 25 ml) in the presence of 3 (1.30×10^{-6} -- 5.00×10^{-6} mol), where the reaction mixture was stirred by a screw propeller rotating at 700 rpm, at which the stirring speed had been confirmed to be no more rate limiting. Kinetics of formation of the azo dye was followed by monitoring the absorbance at 430 nm at 25°C. Apparent first-order kinetic plots covering at least one half-life of the diazophile were obtained with correlation coefficient (γ) greater than 0.99. Apparent k_1 thus obtained were directly proportional to the catalyst concentration with γ of 0.998 in its range from 5.20×10^{-5} to 2.00×10^{-4} $\mathrm{mol.l^{-1}}$, and the gradient of correlation line gave the overall second-order rate constant of 8.9 $\mathrm{mol^{-1}.l.sec^{-1}}$ in the present PTC system.

In connection with azo coupling in liquid-liquid two-phase systems, remarkable accereration of the reaction rate was observed in less polar organic phase; *e.g.* in the azo coupling of 1 with 2 in wet chloroform in the presence of 3, pseudo-first-order rate constant (k_1') of 3.0×10^{-2} $\mathrm{sec^{-1}}$ at 25°C was obtained at 4.0×10^{-4} $\mathrm{mol.l^{-1}}$ of 2, while k_1' at the equal concentration of 2 in aqueous buffer (pH 7.02) was obtained to be 6.0×10^{-5} $\mathrm{sec^{-1}}$ from kinetic data measured separately without 3. Thus, the efficacy of TFPB as phase transfer catalyst is presumably due to the increased dissolution of diazonium ion into a less polar organic phase to result in not only higher concentration but enhanced electrophilicity of the reagent.5)

References and Notes.

1) For example, a) C. M. Starks and C. Liotta, "Phase Transfer Catalysis", Academic Press, New York (1978); b) E. V. Dehmlow and S. S. Dehmlow, "Phase Transfer Catalysis", Verlag Chemie, Weinheim (1980).
2) Sodium TFPB gave satisfactory elemental analyses consistent with $C_{32}H_{12}F_{24}BNa.2.5H_2O$. Synthesis and physico-chemical properties were partly presented at the Sixth Symposium on Fluorine Chemistry in Tokyo (1980).
3) *cf.* M. Ellwood, J. Griffiths, and P. Gregory, *J. Chem. Soc., Chem. Commun.*, 1980, 181.
4) Ref. 1a), p. 37.
5) P. N. Juri and R. A. Bartsch, *J.Org. Chem.*, 45, 2028 (1980).

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