

Synthesis, Lipophilicity, and Stability of Tetrakis (pentafluorophenyl) borate (FTPB) Anion under Highly Acidic Conditions in Comparison with Those of Tetrakis (3,5-bis (trifluoromethyl) phenyl) borate (TFPB) Anion

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Synthesis, Lipophilicity, and Stability of Tetrakis(pentafluorophenyl)borate (FTPB) Anion under Highly Acidic Conditions in Comparison with Those of Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) Anion

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An improved synthetic method for tetramethylammonium **FTPB** by a metal-halogen exchange reaction of pentafluorophenyl bromide with magnesium in the presence of a catalytic amount of butyl bromide and by a subsequent reaction with boron trifluoride diethyl ether was developed. The lipophilicity of tetramethylammonium **FTPB** in a range of hydrophobic organic solvents and its stability under highly acidic conditions were investigated in comparison with those of tetramethylammonium **TFPB**.

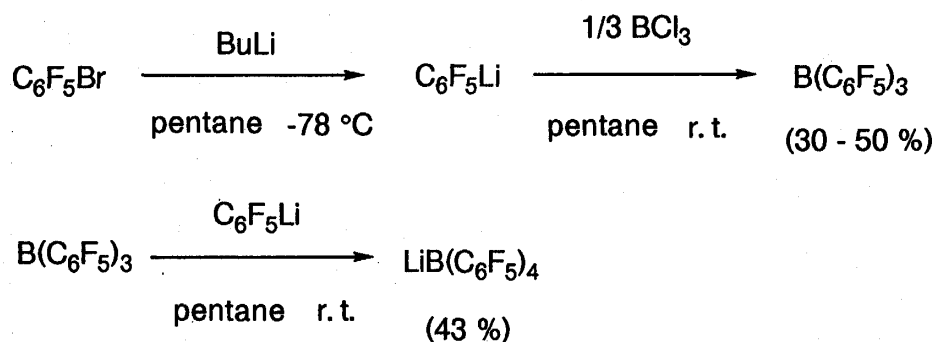
Tetraphenylborate anions with many fluoro and trifluoromethyl substituents on the phenyl groups have received widespread attentions as large and non-coordinating (or weakly coordinating) anions.¹⁻³ Among them tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**TFPB**) anion has been extensively used as an anionic phase-transfer catalyst.⁴ Most recently **TFPB** and tetrakis(pentafluorophenyl)borate(**FTPB**) anions are applied as the effective counterions in homogeneous olefin polymerization catalysts to stabilize highly reactive and base-free cationic metallocene complexes.⁵ Much of this interest stems from their increased stability in acidic and oxidative conditions and their lower tendency to π -coordinate through one of aryl groups compared to those of tetraphenylborate(**TPB**). This is due to lower electron density in the vicinity of the carbon-boron bonds induced by the electron-withdrawing fluoro-substituents which reduces the susceptibility toward electrophilic attack. Indeed **TFPB** is inert to the hydrolysis in the aqueous methanolic sulfuric acid conditions where **TPB** is hydrolyzed with a half-life of less than 30 min.⁶

Although various applications of **TFPB** and **FTPB** have been independently reported in recent works,⁷ there has been no report to compare the physico-chemical properties of these borate anions. In the course of our comprehensive study on the lipophilic and stable organic anions with a large number of polyfluoro-substituents, we report here an improved synthesis of **FTPB** by applying our method developed for the synthesis of **TFPB** and related derivatives,⁸ the lipophilicity and stability under highly acidic conditions of tetramethylammonium salt of **FTPB** in comparison with those of **TFPB**. Furthermore we report some results of our computational calculations to investigate the comparative stability of these borate anions under acidic conditions.

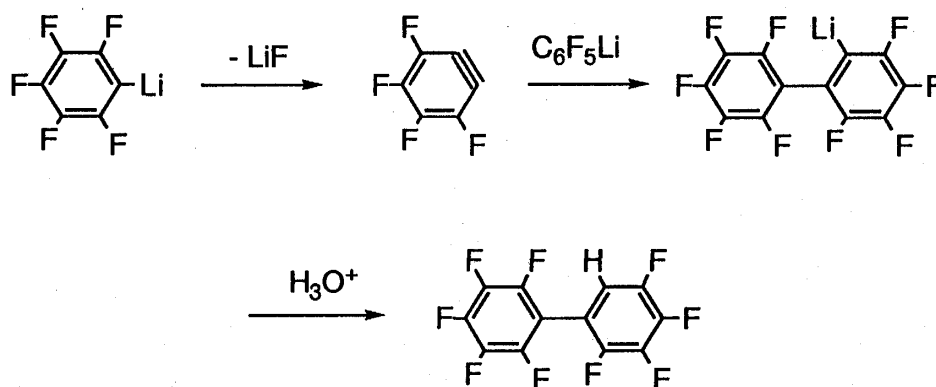
Results and Discussion

Improved Synthesis of Tetramethylammonium FTPB

Lithium **FTPB** was first prepared in 1964 by Massey and Park by a two-step method (Scheme 1).⁹ Tris(pentafluorophenyl) borane has been prepared and isolated in 30-50% yields in the reaction of pentafluorophenyllithium with boron trichloride in pentane. This borane has been treated with pentafluorophenyllithium to give lithium **FTPB** in 20% overall yield. Pentafluorophenyllithium is however well-known to be very labile even at 0 °C to give tetrafluorobenzene, by β -elimination of lithium fluoride, which couples further with pentafluorophenyllithium to yield biphenyl-type compounds (Scheme 2).¹⁰ This instability of pentafluorophenyllithium might have caused the low yields of tris(pentafluorophenyl) borane and lithium **FTPB** in Scheme 1.

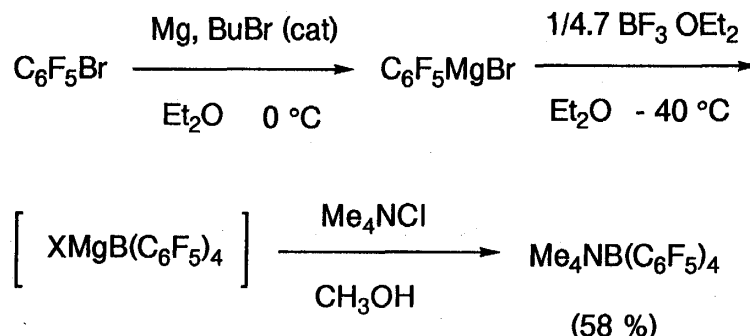


Scheme 1



Scheme 2

In order to improve the yield of **FTPB** we came to an idea to use a metal-halogen exchange reaction as used in our synthesis of **TFPB** and its derivatives.⁸ In Scheme 3 pentafluorophenylmagnesium bromide, which was prepared *in situ* from the equimolar amounts of pentafluorophenyl bromide and magnesium metal in ether in the presence of 10 mol % of butyl bromide, was added to an ether solution of about one fifth molar amount of boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) at $-40\text{ }^\circ\text{C}$. **FTPB** was isolated as tetramethylammonium salt in 58% overall yield based on $\text{BF}_3 \cdot \text{OEt}_2$.



Scheme 3

In this improved method the separation of the ether solution of pentafluorophenylmagnesium bromide from residual magnesium metal and the slow addition of the Grignard reagent into the ether solution of $\text{BF}_3 \cdot \text{OEt}_2$ at low temperature were very important to isolate a crystalline precipitate of tetramethylammonium **FTPB**. Inverse addition of the ether solution of $\text{BF}_3 \cdot \text{OEt}_2$ into the Grignard solution with the residual magnesium metal always resulted in the formation of complex reaction mixture and, consequently, the isolation of the crystalline product was impossible even after repeated chromatographic separation as in the cases of **TFPB** and its derivatives.⁸

Lipophilicity of Tetramethylammonium Salts of **FTPB** and **TFPB**

Lipophilicity is one of the most important properties for an efficient ion-pair extracting agent. We have demonstrated a remarkable substituent effect of trifluoromethyl groups on the lipophilicity of alkali metal salts of **TFPB**.⁶ Further investigation of the relationship between the lipophilicity of tetraarylborates anions and the structure of various fluoro-substituents has indicated that a larger number of trifluoromethyl groups covering the molecular surface of the borate anions increases the solubilities of the borate salts in 1, 2-dibromotetrafluoroethane ($\text{CBrF}_2\text{CBrF}_2$).⁸ As a parameter of lipophilicity we measured the solubilities of tetramethylammonium salts of **FTPB** in dichloromethane, chloroform, and $\text{CBrF}_2\text{CBrF}_2$ in comparison with **TFPB**. Table 1 shows that the solubility of **FTPB** was lower than that of **TFPB** in all of the solvents; namely, two trifluoromethyl groups at *meta* positions are more effective than pentafluoro groups to increase the lipophilicity of **TPB**. Notably the solubility of **FTPB** in $\text{CBrF}_2\text{CBrF}_2$ was very low (less than $3 \times 10^{-7} \text{ mol dm}^{-3}$) compared with that of **TFPB** ($1.4 \times 10^{-5} \text{ mol dm}^{-3}$) even though the molecular surface of **FTPB** anion is covered by a large number of fluoro-substituents.

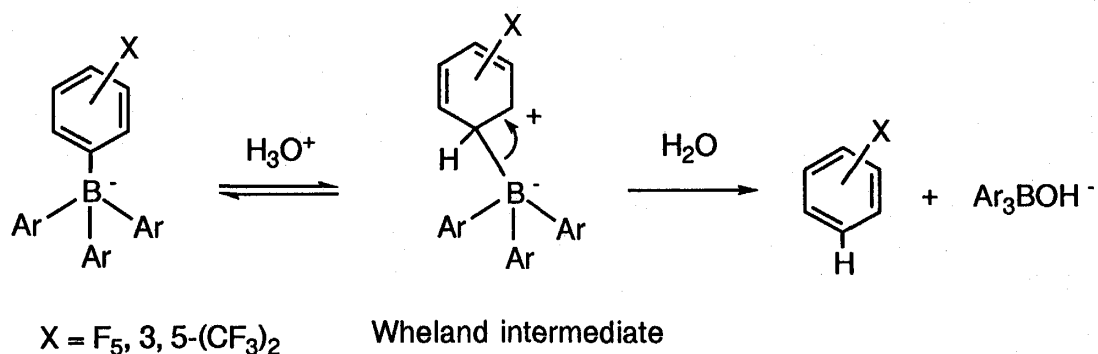
Table 1. Solubilities of Tetramethylammonium **TFPB** and **FTPB** in Hydrophobic Organic Solvents

Borate Anion	Solubility $\times 10^5 / \text{mol dm}^{-3}$		
	CH_2Cl_2	CHCl_3	$\text{CBrF}_2\text{CBrF}_2$
TFPB	2000 ^{a)}	14 ^{a)}	1.4 ^{a)}
FTPB	740	5.4	< 0.03

a) Taken from Ref. 8.

Stabilities of Tetramethylammonium Salts of TFPB and TFPB under Highly Acidic Conditions

The chemical stability of tetraarylborate anions under acidic conditions is another important property for their applications in the anionic phase-transfer catalysis and the homogeneous metallocene complex catalysis, since the reactive species and primary products ion-paired with the borate anions in these reactions are highly electrophilic cationic species. Acid-catalyzed hydrolysis of tetraarylborate anions is known to proceed via a Wheland type intermediate to give a substituted benzene derivative with a rate-determining protonation of the tetraarylborate anions (Scheme 4).¹¹



Scheme 4

Both of tetramethylammonium **TFPB** and **FTPB** salts remained intact in an homogeneous methanol-10.8 mol dm⁻³ sulfuric acid (2/1 v/v) solution at room temperature even after one week. The decomposition of tetramethylammonium TFPB and FTPB salts in an homogeneous methanol-conc. sulfuric acid (6/4 v/v) solution at 25 °C was followed by monitoring the decrease in ¹⁹F-NMR signal intensities due to the remaining tetraarylborates, where 57% of **TFPB** decomposed after 146 h but **FTPB** remained intact even under such acidic conditions. On the other hand, the second-order rate constants were obtained in the decomposition of **TFPB** and **FTPB** anions under dichloromethane-conc. sulfuric acid two-phase conditions at 25 °C by monitoring the formation of acid-catalyzed decomposition products, 1,3-bis(trifluoromethyl)benzene and pentafluorobenzene, respectively, by gas-chromatography (Table 2 and Experimental). Under these two-phase conditions, the activity of oxonium ion incorporated into dichloromethane phase by the borate ion is extremely increased because of dehydration to promote the decomposition of the counter borate ion.¹² Actually **FTPB** gradually decomposed only under these highly acidic two-phase conditions with a half life (τ) of 7.9 h, which was more durable than **TFPB** with a half life of 1.1 h.

Table 2. Second-Order Rate Constants for Decomposition Reactions of Tetramethylammonium **TFPB** and **FTPB** under CH₂Cl₂-Conc. Sulfuric Acid Two-Phase Conditions

Borate Anion	[Ar ₄ B ⁻] ₀ /mol dm ⁻³	$k \times 10^3$ /sec mol dm ⁻³	τ /h
TFPB	1.8 x 10 ⁻³	138	1.1
FTPB	2.1 x 10 ⁻³	17	7.9

Table 3. Heats of Formation (ΔH_f) and Total Energies (ΔE) of Components (5)–(8) and Reaction Enthalpies ($\Delta\Delta H$) of Isodesmic Reactions (2)^{a)}

Component	Method	ΔH_f /kcal mol ⁻¹	ΔE / au ^{b)}	$\Delta\Delta H$ / kcal mol ^{-1c)}
5	MNDO/AM1	10.59		2.47
6	MNDO/AM1	-288.49		
7	MNDO/AM1	-192.05		
8	MNDO/AM1	-83.38		
5	RHF/STO-3G		-715.531989	9.85
6	RHF/STO-3G		-889.825630	
7	RHF/STO-3G		-715.169458	
8	RHF/STO-3G		-890.172416	
5	RHF/3-21G//3-21G		-721.239926	-8.86
6	RHF/3-21G//3-21G		-897.048380	
7	RHF/3-21G//3-21G		-720.992226	
8	RHF/3-21G//3-21G		-897.310246	
5	RHF/6-31G*//3-21G		-725.193599	-1.47
6	RHF/6-31G*//3-21G		-897.048380	
7	RHF/6-31G*//3-21G		-724.917032	
8	RHF/6-31G*//3-21G		-902.219131	

a) Heats of formations for MNDO/AM1 and total energies of the components for the RHF/STO-3G, RHF/3-21G//3-21G, and RHF/6-31G*//3-21G basis sets are evaluated at their optimized geometries. b) One hartree (au) = 625.41 kcal mol⁻¹. c) $\Delta\Delta H = \Delta H_f(7) + \Delta H_f(8) - \Delta H_f(5) - \Delta H_f(6) = \Delta E(7) + \Delta E(8) - \Delta E(5) - \Delta E(6)$.

It is notable that the reaction enthalpies at MNDO/AM1 and RHF/STO-3G level calculations are positive, namely, 2.47 and 9.85 kcal mol⁻¹, respectively, as in the case of the isodesmic reaction (1), while the RHF/3-21G//3-21G and RHF/6-31G*//3-21G level calculations give negative values, -8.86 and -1.47 kcal mol⁻¹, respectively. These results indicate that the low level semi-empirical MNDO/AM1 and RHF/STO-3G methods are not satisfactory for calculating the reaction enthalpy of the isodesmic reactions for these kinds of polyfluorinated compounds and only the higher level *ab initio* calculations are suitable for estimating the relative electronic effect of the polyfluoro-substituents. A failure of MNDO methods for calculating the electronic structures of fluorinated carbon compounds has been recently reported.¹³

We are now continuing further computational investigation of the polyfluoro-substituent effects on the electronic structures, the lipophilicities, and the stabilities of various carbon compounds under highly acidic and oxidative conditions.

Experimental

¹H and ¹⁹F-NMR were recorded on the corresponding spectrometers in similar manners as described previously.⁸ Electronic spectra were measured with a HITACHI 200-20 instrument. Pentafluorophenyl bromide, pentafluorobenzene and 1,3-bis(trifluoromethyl)benzene are commercially available. The synthetic procedure of tetramethylammonium **TFPB** was described previously.⁸

All of computational calculations were done by using SPARTAN System (V. 3.0) on IBM RS/6000-380 Power Station.

Synthesis of tetramethylammonium tetrakis(pentafluorophenyl) borate (TFPB)

Step (1); preparation of Grignard reagent: butyl bromide (0.52 g, 3.73 mmol) was added into ether (10 ml) containing magnesium (0.89 g, 36.6 mmol) under argon atmosphere, to form butylmagnesium bromide. Into the resulting mixture containing butylmagnesium bromide and magnesium was added dropwise an ethereal solution (10 ml) of pentafluorophenyl bromide (9.16 g, 37.1 mmol) at 0 °C and the mixture was then kept stirred at 0 °C for additional 4 h to generate the corresponding Grignard reagent by metal-halogen exchange.

Step (2); Grignard reaction: A supernatant solution of the Grignard reagent was separated from residual magnesium metal by a syringe and dropped into boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) (108 g, 7.89 mmol) in ether (5 ml) at -40 °C under acetonitrile-liq. nitrogen bath, and the reaction mixture was stirred at 0 °C for 7 h and at room temperature for additional 26 h. The reaction was quenched by the addition of saturated aqueous sodium carbonate solution. Precipitates were separated by filtration and an aqueous layer of the filtrate was extracted by ether. The ethereal layer and extracts were combined, washed with saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. Into a darkbrown oily residue (4.61 g) obtained by evaporating the ethereal reaction mixture was added tetramethylammonium chloride (1.0 g, 9 mmol) in methanol. After the mixture was sonicated and methanol was evaporated, water and dichloromethane were added to a residual mixture. By adding hexane into the dichloromethane layer tetramethylammonium **FTPB** was precipitated as a white solid (3.25 g, 4.32 mmol) in a 58% overall yield (based on $\text{BF}_3 \cdot \text{OEt}_2$), melted at temperature higher than 300 °C with decomposition. $\lambda_{\text{max}}(\epsilon)$ (CH_3CN): 259 nm (1100); ^1H NMR ($\text{CD}_3\text{CN}/\text{TMS}$): $\delta = 3.08$ ppm (s, 12H, $\text{N}(\text{CH}_3)_4$). ^{19}F NMR ($\text{CD}_3\text{CN}/\text{C}_6\text{H}_5\text{CF}_3$): $\delta = -70.42$ ppm (s, br, 8F, ortho F), -100.70 ppm (t, $J = 22\text{Hz}$, 4F, para-F), -105.08 ppm (m, 8F, meta-F). The chemical shifts and spectra patterns of ^{19}F NMR of tetramethylammonium **FTPB** are quite similar to those of lithium **FTPB**¹⁴ and metallocene complexes of **FTPB**.^{5f}

A direct preparation of the Grignard reagent with pentafluorophenyl bromide and magnesium metal without butyl bromide in ether at room temperature, and a subsequent inverse addition of $\text{BF}_3 \cdot \text{OEt}_2$ into the Grignard solution with remained magnesium metal at -40 °C resulted in the isolation of a very low yield (11%) of tetramethylammonium **FTPB**.

Measurements of solubility of tetramethylammonium FTPB

A relationship between concentration and absorbance at a key band was determined with acetonitrile solution in a range of known concentrations of tetramethylammonium **FTPB**. Molar extinction coefficient ($\epsilon = 1100$) at 259 nm in acetonitrile was calculated from the slope of the linear plot. The concentration of the saturated solutions of the **FTPB** salt in dichloromethane, chloroform, and $\text{CBrF}_2\text{CBrF}_2$ were determined as follows. After evaporating an appropriate amount of the saturated solution (2 ml of dichloromethane solution, 75 ml of chloroform solution and 54.2 ml of $\text{CBrF}_2\text{CBrF}_2$ solution), the residue was dissolved in acetonitrile (3 ml), and the concentration of the original saturated solution was calculated from the calibration line of the acetonitrile solution.

Acid-catalyzed decomposition of tetramethylammonium TFPB and FTPB in homogeneous methanol-sulfuric acid solutions

Tetramethylammonium **FTPB** (14.1 mg, 1.87×10^{-2} mmol) was vigorously stirred in a mixed solution of methanol (10 ml) and 10.8 mol dm^{-3} sulfuric acid (5 ml) at room temperature. ^{19}F NMR of the reaction mixture showed the **FTPB** salt remained intact even after one week. Tetramethylammonium **TFPB** was also stable under the same conditions. On the other hand, when a solution of methanol (6.3 ml) and conc. sulfuric acid (4.13 ml) containing tetramethylammonium **TFPB** (25 mg, 2.67×10^{-2} mmol) and tetramethylammonium **FTPB** (24 mg, 3.17×10^{-2} mmol) was monitored by the total of ^{19}F NMR signal intensities and the decrease in the intensity of the borate anions at 25 °C, the decomposition of 57% of the **TFPB**

salt was observed after 146 h but the **FTPB** salt was remained intact.

Acid-catalyzed decomposition of tetramethylammonium TFPB and FTPB under dichloromethane-conc. sulfuric acid two-phase conditions

A dichloromethane (10 ml) solution containing tetramethylammonium **TFPB** (17 mg, 1.8×10^{-2} mmol), tetramethylammonium **FTPB** (16 mg, 2.1×10^{-2} mmol), and decane (24 mg, 16.9×10^{-2} mmol) was vigorously stirred with conc. sulfuric acid (3 ml) at 25 °C. The formation of acid-catalyzed decomposition products, 1,3-bis(trifluoromethyl)benzene and pentafluorobenzene, respectively, was traced by monitoring the increase in a gas-chromatography peak intensity relative to that of decane as internal standard. The second-order rate constants (Table 3) were calculated according to the following rate equations:

$$-d[\text{Ar}_4\text{B}^-]/dt = k_2[\text{Ar}_4\text{B}^-][\text{H}_3\text{O}^+] = k[\text{Ar}_4\text{B}^-]^2; \tau = 1/k[\text{Ar}_4\text{B}^-]_0$$

where $[\text{Ar}_4\text{B}^-]$ and $[\text{Ar}_4\text{B}^-]_0$ are the concentrations of the borate anion at reaction time t and $t = 0$, respectively; $[\text{H}_3\text{O}^+]$ is the concentration of oxonium ion ion-paired with the borate anion in the organic phase; k_2 and k are the second-order rate constants; τ is the half life.

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