

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Highly Lipophilic Stable Anionic Agent for Solvent-extraction of Cations

Hiroshi NISHIDA, Naoko TAKADA, Masaji YOSHIMURA,[†]

Takaaki SONODA, and Hiroshi KOBAYASHI*

Research Institute of Industrial Science, Kyushu University 86, Kasuga, Fukuoka 816

[†]Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University 39, Kasuga, Fukuoka 816

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Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) anion was highly lipophilic, practically insoluble in water, and durable against acid and oxidants. Partition equilibria of alkali TFPB between water and organic solvents and the stability in acid media are described and compared with the properties of the parent tetraphenylborate and of some fluorine-containing homologues.

Tetraphenylborate (TPB) (1) anion has a unique structure in which four phenyl groups are tetrahedrally bonded to the central boron atom of univalent negative charge.¹⁾ The charged center is shielded by bulky lipophilic phenyl groups from the medium and no hydrophilic sites are present on the outside of the molecule. 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 atom is exposed into the surrounding medium and provides a strongly hydrophilic center. The relationship is just like that between a quaternary ammonium ion and less substituted ones, though the charge is opposite.

TPB anion forms hydrophobic ion pairs with various univalent cations, such as heavy alkali metals. By taking advantage of this property, TPB has been successfully applied as an ion-pairing agent to precipitation and solvent extraction of various organic and inorganic cations in aqueous solutions.²⁾

One thing to be noticed is that TPB anion is chemically labile, especially in the presence of acids or oxidants.^{3–8)} This reagent must, therefore, be stored and used under strictly limited conditions. In the last two decades, several attempts have been made to overcome the drawback of chemical lability and at the same time to modify the physicochemical properties of TPB.^{9–11)}

Among them, tetrakis(*m*-trifluoromethylphenyl)borate (2) and the *p*-trifluoromethyl homologue (3) are

worthy of attention. The strongly electron-withdrawing effect caused by the trifluoromethyl substituents would suppress the electrophilic attack by proton on to the phenyl-ring carbon ipso to the boron to increase the stability against acids.⁹⁾ And the hydrophobic fluorocarbon moieties would decrease the solubility of the ion pairs in an aqueous solution to promote the precipitate formation and the extraction into the organic solvent.¹²⁾

On the basis of these presumptions, the structure of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) (4) was designed. Convenient preparations of the fluorinated TPB derivatives including TFPB and their properties were roughly reported.¹³⁾ This paper describes detailed examinations of the chemical stability and lipophilicity of TFPB. Preparation of TFPB according to the scheme of Fig. 1 is briefly described in the experimental section. The alkali metal salts of TFPB were practically insoluble in cold water, while being slightly soluble in hot water and readily dissolved in ethanol, ether, and acetone, and to a less extent in chloroform, dichloromethane, and toluene.

Results and Discussion

Chemical Stability. The increased chemical stability of TFPB (4) is noteworthy. The acid-catalyzed degradations of TPB (1), TFPB (4), and related fluorinated derivatives, (2) and (3), were kinetically followed. The decrease of the parent borate in aqueous methanol was monitored by HPLC and ¹⁹F-NMR in the presence of a large excess of sulfuric acid. Respective pseudo-first-order kinetic plots gave good linear relationships. The rate constants in 63% aq methanol are compared in Table 1. Provided the reaction rate is regarded as a first-order dependence on the acid concentration,³⁾ the stability in acid media can be compared in terms of the relative half-life period. The comparison shows that

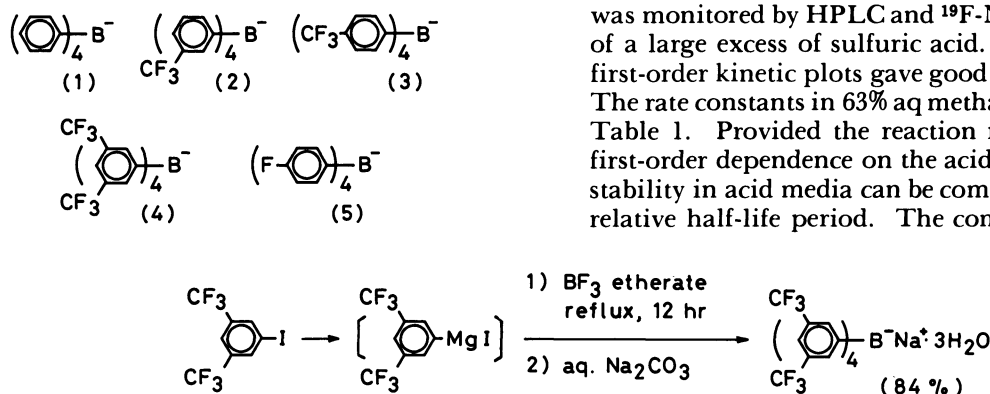


Fig. 1. Preparation scheme of TFPB.

TABLE 1. COMPARISONS OF ACID-CATALYZED DECOMPOSITION RATES OF TETRAARYLBORATES IN AQUEOUS METHANOL (METHANOL : WATER = 67 : 37)

Tetraarylborates	$\frac{[\text{H}^+]}{([\text{H}_2\text{SO}_4] \times 2)}$ mol dm ⁻³	k_{obsd} s ⁻¹	$k_2 = k_{\text{obsd}}/[\text{H}^+]$ s ⁻¹ mol ⁻¹ dm ³	Relative half-life period
(1)	0.049	4.00×10^{-4}	8.00×10^{-3}	1
(2)	2.1	5.19×10^{-7}	2.47×10^{-7}	3.24×10^4
(3)	2.1	3.46×10^{-7}	1.65×10^{-7}	4.85×10^4
(4)	2.1	No decomp.	—	(Unmeasurable)
	8.2	No decomp.	—	

the trifluoromethylation on to the pendent phenyl rings increases the durability against acid to a striking extent. This extent was outstanding in TFPB; it showed no trace of decomposition after standing for one month in 4.1 mol dm⁻³ aq methanolic sulfuric acid at room temperature. The result was the same even when the sample was heated under reflux in 3.6 mol dm⁻³ methanolic sulfuric acid for 7 d.

If one assumes that electrophilic attacks by protons on to the phenyl-ring carbons ipso to the boron are correlated with the σ^+ value of trifluoromethyl groups,⁹ the half-life period of TFPB can be estimated from an extrapolation of the log k_2 - σ^+ plottings¹⁴ of the upper three lines in Table 1, to be approximately 8000 d at 25 °C. This means that the reaction of TFPB takes 100 d to decompose 1% of the initial amount which might be an extent detectable by the present analytical method.

Under aerated conditions, oxidative degradation of TPB (1) and the trifluoromethylated derivatives (2), (3), and (4), were monitored by HPLC in a water-dichloromethane two-phase system. Decay curves are shown in Fig. 2. With the progress of oxidative degradation, two new peaks appeared in HPLC of the organic phase. These increased their peak areas as that of the parent borate peak decreased. One of the new peaks were assigned to the corresponding phenol and the other to the biphenyl. Although the stepwise degradation could not be differentiated, the *m*- and *p*-trifluoromethyl derivatives, (2) and (3), decomposed within 6 and 2.5 h, respectively, while TPB (1) took 10 h before the complete decomposition under our experimental conditions. The time when the borate peak disappeared corresponded to when those of the decomposition products ceased to increase. TFPB (4), on the other hand, indicated no trace of decomposition after being kept aerated for 21 h under the same conditions. If one takes account of the facts that TPB (1) was mostly partitioned into the aqueous phase, while the trifluoromethylated derivatives, (2), (3), and (4), were partitioned into the dichloromethane phase during the air-oxidation in the present two-phase system, and that the solubility of oxygen in dichloromethane, though unavailable in the literature, might be estimated at about 10 times more than that in water based upon the data of homologous halomethanes at the same temperature,¹⁵ it is obvious that the bis(trifluoromethyl)ation of the pendent phenyl groups enormously increased the durability of the TPB structure against the air-oxidation. TFPB was

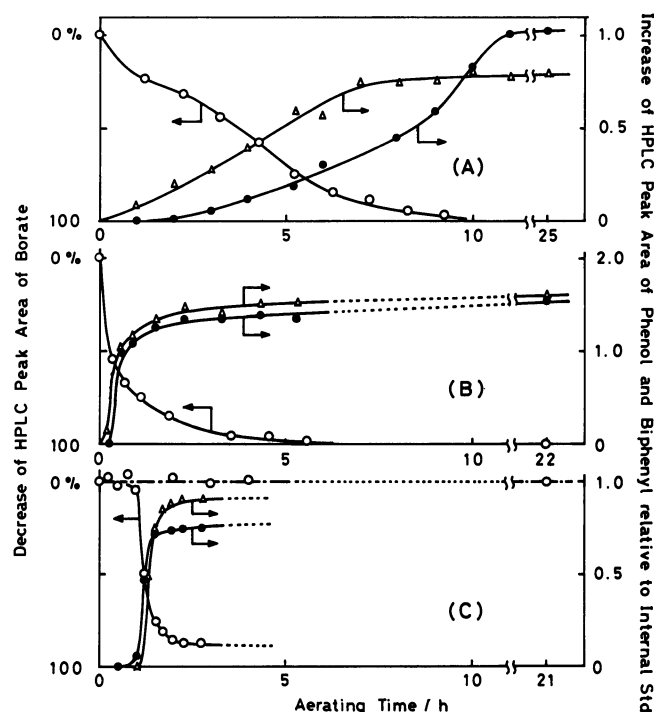


Fig. 2. Decay of the tetraarylborate (○) and occurrence of the corresponding phenol (Δ) and biphenyl (●) upon aeration. (A): TPB (1), (B): *m*-trifluoromethyl deriv. (2), (C): *p*-trifluoromethyl deriv. (3) (—), and TFPB (4) (---).

also durable to a range of oxidants. It remained completely intact even after 22 h 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.¹⁶

Lipophilicity. Partition behaviors of the TFPB ion pairs with alkali metal ions were examined by HPLC in aqueous dichloromethane and aqueous toluene two-phase systems. The organic solvents might be regarded as the representatives of different polarities, and are frequently used as extractants.

Results are summarized in Tables 2 and 3, together with those of some related borates for comparisons.¹³ The ion pairs were generally well extracted into a dichloromethane phase. One may readily notice that the saturated concentrations of alkali TFPB in the dichlo-

romethane phase are about 100 times higher than those of the others; these results indicated it to be highly lipophilic. Toluene was less efficient as an extractant of the ion pairs of such borates, as shown in Table 3. The borate was less soluble in this solvent, and so much remained in the aqueous phase.

Partitions between the two phases can be compared more clearly by their extraction coefficients, K_{ex} , which are given in Table 4. The values of TFPB salts are much higher than those of the others; especially the value of lithium salt was extremely increased. One may say that TFPB combined with toluene shows a somewhat different extraction behavior for alkali metal ions from the other homologues.

Unique behaviors of TFPB at the solvent extraction occurred not only in the partition equilibrium, but also in the phase-transfer rates, which were more than three times faster than that of tetrakis(*p*-fluorophenyl)borate (5), when compared by use of their lithium salts in both dichloromethane–water and toluene–water two-phase systems.¹³⁾

As a conclusion, bis(trifluoromethyl)ation of the pendent phenyl rings of TPB was unexpectedly effective not only in the chemical stabilization of this ion-pairing agent, but also in the increase of solubility of its ion pairs in organic solvents and in the acceleration of the extraction rate. Also, the extraction coefficients varied depending upon the substituents on the pendent

TABLE 2. PARTITION OF ALKALI TETRAARYLBORATES BETWEEN AQUEOUS AND DICHLOROMETHANE PHASES

Tetraarylborates		Concn. of alkali tetraarylborate/mol dm ⁻³				
		Li	Na	K	Rb	Cs
(1)†	aq	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶
	org	3.0×10 ⁻⁵	1.0×10 ⁻⁵	5.5×10 ^{-6*}	4.0×10 ^{-6*}	1×10 ^{-5*}
(5)†	aq	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶
	org	3.9×10 ⁻⁵	5.0×10 ⁻⁴	2.6×10 ⁻⁴	9.5×10 ⁻⁵	1.7×10 ⁻⁴
(2)†	aq	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶	<10 ⁻⁶
	org	3.0×10 ⁻⁵	7.0×10 ⁻⁵	7.0×10 ⁻⁵	5.0×10 ⁻⁵	3.1×10 ⁻⁵
(4)	aq	5.6×10 ⁻⁷	5.8×10 ⁻⁶	5.8×10 ^{-7*}	2.0×10 ^{-7*}	1.7×10 ^{-7*}
	org	1.3×10 ⁻³	3.4×10 ⁻³	1.5×10 ^{-3*}	5.5×10 ^{-4*}	1.6×10 ^{-3*}

*, Occurrence of precipitates. †, Concentration in the aqueous phase was below the detection limit (10⁻⁶ mol dm⁻³) of the spectrophotometric method.¹⁷⁾

TABLE 3. PARTITION OF ALKALI TETRAARYLBORATES BETWEEN AQUEOUS AND TOLUENE PHASES

Tetraarylborates		Concn. of alkali tetraarylborate/mol dm ⁻³				
		Li	Na	K	Rb	Cs
(1)	aq	4.5×10 ⁻⁴	4.3×10 ⁻⁴	<10 ^{-6*}	1.0×10 ^{-6*}	<10 ^{-6*}
	org	1.4×10 ⁻⁵	8.5×10 ⁻⁶	5.0×10 ^{-6*}	5.5×10 ^{-5*}	1×10 ^{-5*}
(5)	aq	4.3×10 ⁻⁴	4.3×10 ⁻⁵	9.1×10 ⁻⁵	5.2×10 ^{-5*}	<10 ^{-6*}
	org	1.5×10 ⁻⁵	1.0×10 ⁻⁵	9.5×10 ⁻⁶	6.5×10 ^{-6*}	1×10 ^{-5*}
(2)	aq	7.2×10 ⁻⁶	5.3×10 ⁻⁵	8.7×10 ^{-6*}	6.2×10 ⁻⁶	<10 ^{-6*}
	org	1.4×10 ⁻⁵	1.6×10 ⁻⁵	2.5×10 ^{-4*}	3.3×10 ⁻⁴	3.5×10 ^{-4*}
(4)	aq	5.3×10 ⁻⁷	5.7×10 ⁻⁷	~2×10 ⁻⁸	~2×10 ⁻⁸	~2×10 ⁻⁸
	org	1.4×10 ^{-4*}	6.4×10 ^{-5*}	<DL*†	<DL*†	<DL*†

*, Occurrence of precipitates. †, Concentration in the organic phase was below the detection limit (DL) (1.6×10⁻⁷ mol dm⁻³) of the present HPLC method.

TABLE 4. EXTRACTION COEFFICIENTS, K_{ex} , OF ALKALI TETRAARYLBORATES IN THE TWO-PHASE SYSTEMS, WHERE $K_{ex} = [MB]_{org}/[M^+]_{aq}[B^-]_{aq}$

Tetraarylborates	Two-phase system	Alkali ion				
		Li	Na	K	Rb	Cs
(1)	(A)	0.31	0.20	>50	550	—
(5)	(A)	0.35	23	1.0	1.3	—
(2)	(A)	0.19	3.0	2.9	5.3	—
(4)	(A)	2.5×10 ³	1.3×10 ³	—	—	—
	(B)	2.4×10 ⁴	6.1×10 ³	2.5×10 ⁴	2.7×10 ⁵	9.3×10 ⁴

(A), Water–toluene system. (B), Water–dichloromethane system.

phenyl rings and the kinds of organic extractants. This result suggested the possibility of selective solvent-extraction for certain organic and inorganic cations by use of a proper organic extractant combined with an ion-pairing agent.

Further studies along this line are now being undertaken in this laboratory.

Experimental

^1H - and ^{19}F -NMR spectra were obtained on a JEOL FX-100 and Hitachi R-24B-F instruments in reference to the internal TMS and trifluoroacetic acid, respectively, unless otherwise described. HPLC charts were recorded on a Hitachi 380-30 liquid chromatograph combined with a spectrophotometric detector and a Shimadzu recording integrator C-R1A Chromatopac. A separating column 500 mm long was packed with Hitachi gel 3010. Methanol was an efficient eluant unless otherwise stated. Sodium tetraphenylborate (1) (Dotite Kalibor®) and sodium tetrakis(*p*-fluorophenyl)borate (5) (Dotite Cesibor®) were commercially available reagents. Sodium tetrakis(*m*-trifluoromethylphenyl)borate (2)⁹ and the *p*-trifluoromethyl homologue (3)⁹ were prepared in this laboratory.¹³

Preparation of Sodium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (4). An ethereal solution of boron trifluoride (365 mg, 2.52 mmol) was added dropwise over 40 min into an ethereal solution of 3,5-bis(trifluoromethyl)phenylmagnesium iodide, which was prepared from 1-iodo-3,5-bis(trifluoromethyl)benzene (4.78 g, 14.06 mmol), magnesium turnings (0.42 g, 17.1 mmol) and anhydrous ether (13 cm³). The mixture was, after being refluxed for 12 h, poured portionwise into aqueous sodium carbonate (24.0 g in 100 cm³ of water) with vigorous stirring. The precipitated magnesium carbonate was filtered off and washed with ether. The aqueous layer of the filtrate was separated from the ethereal one, saturated with sodium chloride, and extracted repeatedly with ether. All the ethereal extracts were combined with the initial ethereal layer, and evaporated under reduced pressure. The residual solid was successively eluted from a silica-gel column with hexane, dichloromethane, and methanol. The borate was isolated in the form of hydrated sodium salt from the dichloromethane and methanol fractions. The yield was 2.0 g (84%). IR (KBr): 3500, 1350, 1280, and 1200–1100 cm⁻¹. ^{19}F -NMR (CH₃OH): 13.52 ppm (m), and ^1H -NMR (CDCl₃-DMSO-*d*₆): 7.50–7.70 (m) and 2.95 (s).

Hot aqueous tetraethylammonium iodide was added to a saturated hot aqueous solution of the sodium TFPB to yield colorless precipitates, which were successively eluted from a silica-gel column with hexane, benzene, ether, and methanol. The solid residue, which was obtained from the ether and methanol fractions by evaporation, was washed with cold chloroform to give the tetraethylammonium salt, mp 181–182 °C. IR (KBr): 1350, 1280, and 1200–1100 cm⁻¹. λ_{max} (ϵ): 269 (4100) and 278 nm (3200). ^1H -NMR (CDCl₃-DMSO-*d*₆): 1.25 (tt, *J*=2 and 7 Hz, -CH₃, 12H), 2.75 (s, H₂O), 3.20 (q, *J*=7 Hz, -CH₂-, 8H), and 7.50–7.70 (m, aromatic, 12H). Found: C, 48.25; H, 3.23; N, 1.33%. Calcd for C₄₀H₃₂NF₂₄B; C, 48.36; H, 3.27; N, 1.09%.

Kinetics of Acid Decomposition of the Trifluoromethylated Derivatives. A methanol solution (0.3 cm³) of the trifluoromethylated compound (2, 3, or 4) (*ca.* 20 mg) and the required amount of aqueous sulfuric acid were combined in an NMR tube at a lowered temperature and then kept at 25 °C in a thermostat. The intensity change in ^{19}F -NMR signals of the parent borate and those of the decomposition products were followed at specified intervals.

The signal of the *m*-trifluoromethyl compound (2) at 14.2 ppm diminished with the increments of those of the corresponding decomposition products at 13.8, 13.7, and 13.4 ppm. The signal of the *p*-trifluoromethyl compound (3) at 14.7 ppm and those of the decomposition products at 14.0, 13.6, and 13.4 ppm changed in a similar manner.

On the condition that the total peak area of ^{19}F -NMR signals were unchanged throughout the reaction, the logarithm of relative peak area of the parent compound was plotted against the reaction time to give a good linear relationship with a correlation coefficient (γ) more than 0.99 at least over one half-life period. The gradient of the correlation line gave a pseudo-first-order rate constant, k_{obs} . The apparent second-order rate constant, k_2 , was derived according to the equation, $k_2 = k_{\text{obs}}/[\text{H}^+]$, where $[\text{H}^+]$ means the acid concentration.

Kinetics of Acid Decomposition of TPB. An aqueous solution of TPB (6.82×10^{-2} mol dm⁻³, 8.5 cm³), aqueous sulfuric acid (0.123 mol dm⁻³, 10.0 cm³) and methanol (31.5 cm³) were combined in a stoppered flask, and the resulting solution was kept at 25 °C in a thermostat. An aliquot (0.50 cm³) was taken out of the solution at 10 min intervals and neutralized with aqueous sodium hydroxide (0.0815 mol dm⁻³, 0.35 cm³). A sample of 40 mm³ from the aliquot was analyzed by HPLC at 266 nm. Since the chromatographic peak of TPB and those of the degraded borates were not well resolved, the rate constant of the acid decomposition of TPB was derived from the initial rate measured in the linear region (the 50-min period since the beginning) of the pseudo-first-order plotting to be 4.00×10^{-4} sec⁻¹ with γ of 0.998.

Air-oxidation of TPB. A two-phase mixture of an aqueous solution of TPB (5.62×10^{-4} mol dm⁻³, buffered at pH 6.0, 25 cm³) and dichloromethane (25 cm³) was aerated. Every hour, 40 mm³ samples were taken out of the organic and aqueous phases and analyzed by HPLC. TPB and degraded borates were found in the aqueous phase to give an overlapped HPLC peak. The decay curve, consequently, depicted the descending overall area of the overlapped peaks. The resulting phenol and biphenyl were found in the organic phase. Both were assigned by the comparison of their retention time in HPLC and GLC with those of the authentic specimen.

Air-oxidation of the Trifluoromethylated Derivatives. A two-phase mixture of an aqueous solution (20 cm³, buffered at pH 6.0) of the *m*-trifluoromethyl compound (2) (6.05×10^{-4} mol dm⁻³) and a dichloromethane solution (20 cm³) of 4,4'-difluorobiphenyl (2.43×10^{-4} mol dm⁻³ as an internal standard) was aerated. At specified intervals a sample (40 mm³) from the aqueous phase and one (10 mm³) from the organic phase were analyzed by HPLC. The HPLC peak of the parent borate ($t_R=1.3$ min) in the aqueous phase was closely overlapped with those of degraded borates, which were also completely decomposed within 6 h under the experimental conditions, thereafter no HPLC peaks were observed by a photometric detector at 270 nm. The relative increase of the decomposition products ($t_R=2.5$ and 5.3 min) in the organic phase were also followed against the internal standard ($t_R=8.5$ min).

Structures of the decomposition products were assigned with those obtained in a separate air-oxidation experiment by use of 0.80 mmol of the borate. The fraction of $t_R=2.5$ min was assigned tentatively to be *m*-trifluoromethylphenol by GC-MS ($m/z=162$ (M⁺)) and ^{19}F -NMR measurement (a singlet at $\delta=98.89$ ppm downfield from C₆F₆) and ^1H -NMR spectral comparison with that in the literature.¹⁰ The fraction of $t_R=5.3$ min was an unsymmetric bis(trifluoromethyl)biphenyl by GC-MS ($m/z=290$ (M⁺)) and ^{19}F -NMR data (two equal signals of $\delta=99.55$ and 99.42 ppm downfield from C₆F₆).

Air-oxidation of TFPB (4) and the *p*-trifluoromethyl com-

pound (3) were carried out in a similar manner by use of an aqueous buffer (25 cm³, pH 6) and a dichloromethane solution (25 cm³) of the borate and 4,4'-difluorobiphenyl as an internal standard. The remaining parent borate and decomposition products from the *p*-trifluoromethyl compound were found in the organic phase and were determined in a similar manner against the internal standard.

Partition of Alkali TFPB in Organic Solvent-water Two-phase Systems. Typical Procedure. Dichloromethane-water System: A mixture of sodium TFPB (ca. 2×10^{-5} mol), alkali acetate (0.1 mol dm⁻³)-acetic acid buffer (pH 6.0, 250 cm³) and dichloromethane (10.0 cm³) was shaken until equilibrated (2 h) at 30 °C in a thermostat. Added amounts of lithium, sodium, potassium, rubidium, and cesium acetates were each large enough so that sodium ions from sodium TFPB were negligible.

The resulting mixture settled and separated into two layers.

TFPB in the organic layer was determined by HPLC at 270 nm with 40 mm³ of sample in reference to an internal standard (toluene). The eluant was methanol containing 10 v% of water. TFPB in the aqueous layer was extracted from a 200-cm³ portion with 10 cm³ of dichloromethane so that the solute was concentrated 20-fold over the fraction in the aqueous layer, to be determined by HPLC in a similar manner.

Toluene-water System: A mixture of the aqueous buffer (pH 6.0, 800 cm³) containing the acetate of alkali ion to be examined, toluene (25.0 cm³), and sodium TFPB (ca. 5×10^{-6} mol) was equilibrated at 30 °C by 16-h shaking.

TFPB in the toluene phase was determined by HPLC in reference to the internal standard (*o*-cresol). TFPB in the aqueous phase was preconcentrated by extraction and determined by a standard-addition method: The first aliquot (250 cm³) from the aqueous layer was extracted with dichloromethane (7.0 cm³) by 30-min shaking, the 2nd 250 cm³ was done with the same solvent (7.0 cm³) containing 1.21×10^{-7} mol of sodium TFPB, and the 3rd one was done in a similar manner by use of 2.42×10^{-7} mol of sodium TFPB. Each extract was analyzed for TFPB by HPLC with 40 mm³ of sample. Extrapolation of the linear plotting of TFPB peak area against the standard increment of TFPB afforded the analysis of TFPB in the first aliquot.

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