

Notes

Electrochemistry in Benzotrifluoride: Redox Studies in a “Noncoordinating” Solvent Capable of Bridging the Organic and Fluorous Phases

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Introduction

Additions to the inventory of electrochemically useful nonaqueous solvents provide alternatives in which to study the redox chemistry of test molecules.¹ Among solvents that do not coordinate strongly to metals, only chlorohydrocarbons have achieved wide usage for electrochemical investigations of inorganic and organometallic compounds. Although 1,2-difluorobenzene is a useful option,² its adoption has been rather limited, owing perhaps to its expense.³ We now report experiments that show that benzotrifluoride [C₆H₅CF₃, (trifluoromethyl)benzene] provides an attractive alternative in this class of solvents. Benzotrifluoride (BTF) has a dielectric constant at room temperature (9.2) similar to that of dichloromethane (8.9). Its liquid range is –29 to 102 °C, and its viscosity (0.57 mPa s) is about the same as that of THF (0.55). The solvent polarity parameter⁴ of BTF is between those of THF and CH₂Cl₂, and its cost (as reagent-grade) is over 50-fold lower than difluorobenzene.³ Because BTF is relatively nontoxic and environmentally benign, it has replaced either benzene or chlorohydrocarbons in many industrial applications;⁵ its relative inertness has made it an attractive medium for transition-metal-catalyzed reactions.^{5,6} The uncommon miscibility of BTF with both organic and fluorous⁷ solvents has led it to a place of importance in strategies involving synthetic processes and separations in the blossoming area of fluorous phase chemistry.^{5–7}

Supporting electrolyte solutions of 0.1 M in BTF can be prepared using tetrabutylammonium salts of [BF₄][–], [ClO₄][–], or the recently described⁸ [B(C₆F₅)₄][–]; the resistivities of some of these solutions are presented in the Table 1, along with

Table 1. Specific Resistances of Some 0.1 M Tetrabutylammonium Salts in Selected Solvents at Ambient Temperatures in Units of Ω cm

anion	solvent		
	BTF	THF	CH ₂ Cl ₂
[PF ₆] [–]	<i>a</i>	2300	720
[BF ₄] [–]	4300	3400 ^b	800
[ClO ₄] [–]	4800	360 ^c	840 ^d
[B(C ₆ F ₅) ₄] [–]	790	490	470

^a Limited solubility; no measurements made. ^b Literature for 0.5 M, 587 (House, H. O.; Feng, E.; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 2371). ^c Literature for 0.5 M, 583 (House, H. O.; Feng, E.; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 2371). ^d Literature, 725 (Kadish, K. M.; Ding, J. Q.; Malinski, T. *Anal. Chem.* **1984**, *56*, 1741); 800 (Svorstol, I.; Songstad, J. *Acta Chem. Scand. B* **1985**, *39*, 639).

comparative values for other commonly employed electrolyte media. Hexafluorophosphate salts, including [NBu₄][PF₆], do not appear to be very soluble in BTF. Although the lipophilic anion [B(C₆F₅)₄][–] gives the most highly conductive solutions among the electrolytes we tested, resistivity values for solutions of the [BF₄][–] and [ClO₄][–] salts are quite respectable and voltammetric data with [NBu₄][BF₄] are reported in this paper.

Experimental Section

Electrochemical experiments were carried out in a Vacuum Atmospheres drybox under a nitrogen atmosphere containing less than a few ppm oxygen and water.

Reagent grade benzotrifluoride (Aldrich) was distilled under nitrogen at ambient pressure and stored over molecular sieves. Just prior to an electrochemical experiment, the solvent was distilled bulb-to-bulb under static vacuum and then brought into the drybox. Toluene was vacuum-distilled from potassium. Electrochemical glassware was removed from a 110 °C oven and put directly into the antechamber of the drybox. Supporting electrolytes were prepared by standard metathesis methods, recrystallized several times, and dried in vacuo at 100 °C. [NBu₄][B(C₆F₅)₄] was prepared from Li[B(C₆F₅)₄] and [NBu₄]Br as previously described.⁸ Potentials in this paper are referenced to the ferrocene/ferrocenium couple. The experimental reference electrode was a AgCl-coated silver wire in BTF that was separated from the test solution by a fine glass frit. At an appropriate point in the experiment, ferrocene was added to the solution as an internal standard to check the reference potential. A Princeton Applied Research model 173 or model 273 potentiostat interfaced to a personal computer controlled the electrochemical experiments. The potentiostat compliance voltages were 100 V. Low-temperature electrochemical experiments were conducted inside the drybox by immersing the electrochemical cell in a heptane bath that was cooled with a precision of better than 1 °C by an FTS Systems refrigeration probe. Decamethylferrocene, ferrocene, cobaltocene, and nickelocene were purchased from Strem Chemicals. All but the first of these were vacuum-sublimed before use. The complex CpCo(cyclooctadiene), **1**, was prepared as previously described.⁹ 1,4-Benzoquinone (Aldrich) was vacuum-sublimed.

Results and Discussion

The background “window” for distilled BTF (containing 0.1 M [NBu₄][BF₄]) is +2.0 V to –2.8 V vs ferrocene/ferrocenium

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at Pt or glassy carbon electrodes.¹⁰ The processes responsible for the anodic and cathodic breakdowns are most likely the oxidation and reduction reactions, respectively, of BTF itself, which have been reported to occur at $E_{1/2}$ values of about +2.2 and -3.0 V in nonaqueous solvents.¹¹

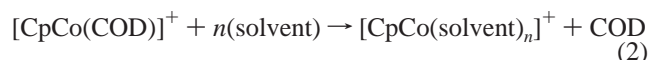
Cyclic voltammetry (CV) scans of decamethylferrocene were diffusion-controlled and chemically reversible ($E_{1/2} = -0.51$ V vs Fc) while exhibiting some apparent ohmic distortion in the tetrafluoroborate electrolyte {e.g., $\Delta E_p = 110$ mV at 1 mm diameter glassy carbon disk, scan rate (ν) = 0.1 V/s, [(C₅Me₅)₂-Fe] = 0.5 mM}. A greater degree of supporting electrolyte dissociation is expected when a large tetrakis(fluoroaryl)borate anion is used;⁸ indeed, in BTF/0.1 M [NBu₄][B(C₆F₅)₄], ΔE_p was 70 mV under the same conditions. A diffusion coefficient of 1.2×10^{-5} cm²/s was measured in the [BF₄]⁻ solution by chronoamperometry. Bulk electrolysis of 1 mM decamethylferrocene proceeded readily in BTF/0.1 M [NBu₄][BF₄] using a standard three-compartment cell separated by two fine frits. An amount of 1.0 F/equiv was passed, and steady-state voltammetry indicated complete conversion to the (green) decamethylferrocenium ion.

The liquid range of BTF can be extended to lower temperatures by employing toluene as a cosolvent. Use of [NBu₄][B(C₆F₅)₄] as the supporting electrolyte ensures reasonable conductivity in such mixtures (see Figure 1 of Supporting Information, which shows the CV of (C₅Me₅)₂Fe at -40 °C in a 2:1 BTF/toluene mixture; $\Delta E_p = 110$ mV at $\nu = 0.1$ V/s).

The absence of nucleophilic functional groups in BTF suggests its use in the generation of organometallic cation radicals. As a test of this hypothesis, the oxidation of (η^5 -C₅H₅)-Co(η^4 -COD) (COD = cyclooctadiene), **1**, was probed in this solvent. Complex **1** is known to undergo oxidation in a one-electron process to a 17-electron monocation **1**⁺,



which is prone to loss of the COD ligand. This loss of diolefin is greatly accelerated by donor solvents in a reaction that yields a solvento-species:



The behavior of this system is typified by the fact that loss of COD is very much slower in CH₂Cl₂ than in THF or CH₃CN.^{9,12}

By measuring the chemical reversibility of the couple **1/1**⁺ (using CV scan rates of 5 V/s > ν > 0.5 V/s) in BTF, we find that the behavior of **1** mimics that observed in CH₂Cl₂, as opposed to that found in donor solvents. A half-life of about 0.6 s was estimated for **1**⁺ in BTF at 272 K ($t_{1/2} \ll 0.01$ s in CH₃CN).^{9,12a}

A further indication of the low nucleophilicity of BTF toward oxidized systems is seen in CV scans of nickelocene. The dication [Cp₂Ni]²⁺ is known to be reactive toward nucleophiles, leading to limited chemical reversibility for the [Cp₂Ni]⁺²⁺

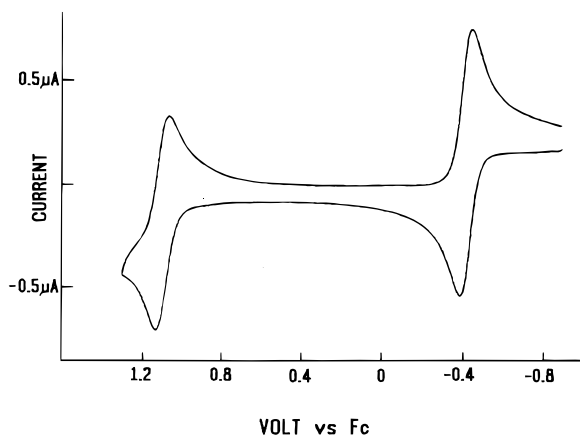


Figure 1. Cyclic voltammetric scan ($\nu = 0.1$ V/s) of 0.5 mM nickelocene in benzotrifluoride containing 50 mM each of [NBu₄][B(C₆F₅)₄] and [NBu₄][BF₄]: $T = \text{ambient}$, 1 mm glassy carbon disk. Shown are two consecutive anodic reactions, the first resulting in [Cp₂Ni]⁺ and the second in [Cp₂Ni]²⁺.

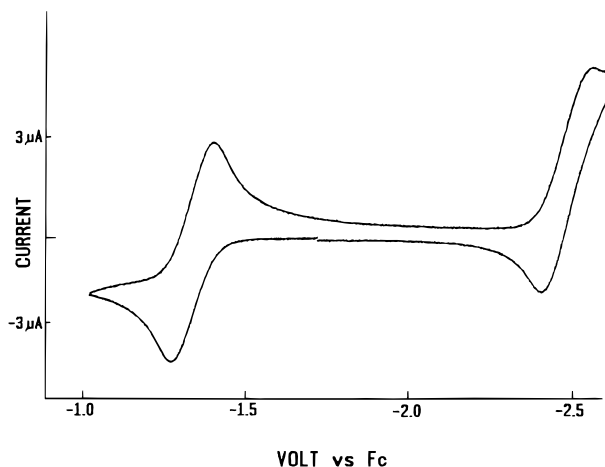


Figure 2. Cyclic voltammetric scan ($\nu = 0.1$ V/s) of 1 mM cobaltocene in benzotrifluoride/0.1 M [NBu₄][B(C₆F₅)₄]: $T = \text{ambient}$, 1.5 mm glassy carbon disk. The scan was initiated at ca. -1.7 V toward more positive potentials. The couple to the left arises from the oxidation of Cp₂Co, the one to the right from its reduction.

couple in solvents such as CH₃CN, particularly when trace water is present.¹³ Two chemically reversible oxidations are seen, however, in BTF, again mimicking the behavior of this compound in CH₂Cl₂^{14a} (Figure 1, $\Delta E_p = 75$ mV, $i_c/i_a = 1.0$ at $\nu = 0.1$ V/s for both waves). $E_{1/2}$ potentials of -0.42 and 1.10 V (vs Fc) were measured, respectively, for the Ni(II)/Ni(III) and Ni(III)/Ni(IV) couples. The separation of these two potentials (by 1.52 V) warrants comment, since much smaller differences have been reported in other media in which both the solvent and the supporting electrolyte anion were different from those used in the present study {0.8–0.9 V in CH₃CN/[NEt₄][ClO₄],¹³ ca. 0.83 V in CH₂Cl₂ with an unspecified electrolyte that was most likely either [NBu₄][PF₆] or [NBu₄][BF₄],^{14a} and 1.1 V in a molten salt^{14b}}. The large decrease in the potential of the Ni(III)/Ni(IV) couples in the previous studies most likely arises from an increase in ion-pairing energies of the nickelocene dication with the various electrolyte anions

(10) The background windows are quoted as the potentials at which a current density of about 0.2 mA/cm² was attained at a glassy carbon electrode; scan rate is 0.1 V s⁻¹. This current density is typical of approximately 1 mM analytes undergoing one-electron processes in this medium.

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employed (e.g., $[\text{ClO}_4]^-$ and $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$). The anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ is expected to associate very weakly with the metallocene dication compared to the $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ anions.^{8,15,16} Indeed, a separation of only about 0.7 V is seen for the two anodic peaks for oxidation of Cp_2Ni in BTF/0.1 M $[\text{NBu}_4][\text{BF}_4]$, though good thermodynamic information is obscured by the apparent precipitation of $[\text{Cp}_2\text{Ni}][\text{PF}_6]_2$ on the electrode surface (see CV in Figure 2 of Supporting Information). A systematic study probing the association constants of metallocene-like cations and polycations with anions traditionally viewed¹⁷ as noncoordinating is underway. Ion-pairing energies may play a determining role in some reaction mechanisms of cationic sandwich complexes in low-polarity media.¹⁸

Whereas BTF will probably find its dominant usage in anodic reactions, reductions may also be studied, although the cathodic range of the solvent is more comparable to that of the chlorohydrocarbons rather than to THF or other difficult-to-reduce solvents. The reductions of both benzoquinone ($E_{1/2} = -1.05$ V vs Fc) and cobaltocenium ($E_{1/2} = -1.35$ V in $[\text{NBu}_4][\text{BF}_4]$ electrolyte, glassy C electrode) are fully chemically reversible at $v = 0.1$ V/s. As shown in Figure 2, the reduction of Cp_2Co to the corresponding monoanion ($E_{1/2} = -2.48$ V) may also be observed, but the redox process is close to the negative potential limit of the solvent. The less-than-full

chemical reversibility of the wave for $[\text{Cp}_2\text{Co}]^{0/-}$ most likely arises from transfer of an electron from the cobaltocenium anion to the solvent, with subsequent regeneration of Cp_2Co . This behavior is similar to that seen in CH_2Cl_2 , again emphasizing the parallel in electron-transfer reactivity between BTF and chlorohydrocarbon solvents. Reduction of BTF through electron-transfer mediators has been reported earlier.¹⁹

Benzotrifluoride is, in summary, a convenient, inexpensive and relatively noncoordinating solvent of low toxicity that is useful for electrochemistry. It should be considered for situations in which metal complexes or their redox products may potentially react with chlorohydrocarbons. It should also prove useful as a medium to facilitate electrochemistry in the expanding area of fluorous-phase chemistry, since BTF is classified as a "crossover" solvent, that is, one having good miscibilities with both organic solvents and fluorous solvents such as perfluoroalkanes. Investigations of such systems are underway.²⁰

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Supporting Information Available: One figure giving a CV scan of decamethylferrocene in toluene/BTF at 233 K and a second figure showing a CV scan of the two oxidation waves of nickelocene in BTF using $[\text{NBu}_4][\text{BF}_4]$ as the supporting electrolyte. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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