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Synthesis and Isolation of a Fullerene Carbocation (C_{76}^+)

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A fundamental characteristic of fullerenes is their inherent electronegativity. They are easily reduced to fulleride anions (e.g., $C_{60}{}^{n-}$) and behave as electrophiles in much of their derivatization chemistry.[1] In contrast, fullerenes are difficult to oxidize. There is evidence from EPR and NMR spectroscopies and nucleophilic trapping experiments for the existence of $C_{60}{}^{n+}$ ions in superacid media, but there is uncertainty about their charge states and stability is tenuous.[2] Photochemical and radiolytic techniques have been used to produce $C_{60}{}^+$ for transient spectroscopic identification.[3] Electrochemical investigations indicate that with the appropriate choice of solvent, fullerene cations can be stable entities on the voltammetric timescale (ca. 1 s).[4,5] However, neither electrochemical nor superacid media lend themselves to the ready isolation of solutes and thus, after this initial activity, efforts to prepare fullerene cations seem to have waned. We now report the development of a reagent that is generally suited to the preparation of highly reactive cations and illustrate its use in the isolation of a $C_{76}{}^+$ salt. The choice of C_{76} over C_{60} or C_{70} was made on the basis of electrochemical oxidation potentials: $E° = +0.81$ V compared to $+1.26$ V for C_{60} and $+1.20$ V for C_{70} ($E°$ are quoted vs the ferrocene/ferrocenium couple $= 0.00$ V; SCE $= -0.31$ V).[5]

The problem of oxidizing fullerenes to fullerene cations is the problem of finding an oxidant strong enough for the task, but one which does not bring along with it a reacting nucleophile. A suitable oxidant of the electron-abstracting type is the radical cation of tris(2,4-dibromophenyl)amine ($E° = 1.16$ V).[6] It is stable and isolable,[6] and its reduction product, the triarylamine, is very weakly nucleophilic for steric and electronic reasons. For a counterion, we have chosen the exceptionally inert hexahalogenated carborane $CB_{11}H_6Br_6{}^-$, possibly the least nucleophilic anion presently known.[7] Thus, the new "electron hole" reagent $[Ar_3N^{\bullet+}][CB_{11}H_6Br_6{}^-]$ was prepared as a green microcrystalline solid by treatment of tris(2,4-dibromophenyl)-amine (Ar_3N) and the silver salt of the carborane[8] with a small excess of bromine in dry dichloromethane (eq 1).

$$\mathrm{Ar_3N + Ag(CB_{11}H_6Br_6) + {}^1/_2Br_2 \xrightarrow{CH_2Cl_2} [Ar_3N^{\bullet+}][CB_{11}H_6Br_6{}^-] + AgBr} \tag{1}$$

Like its $SbCl_6{}^-$ salt,[6] this reagent was characterized by λ_{max} (*o*-dichlorobenzene) at 378, 447, and 880 nm and by a broad EPR signal ($g = 2.0112$, $\Delta H = 37$ G in frozen *o*-dichlorobenzene at 15 K).

Treatment of C_{76} with $[Ar_3N^{\bullet+}][CB_{11}H_6Br_6{}^-]$ in carefully dried, weakly nucleophilic solvents such as *o*-dichlorobenzene or 1,1′,2,2′-tetrachloroethane leads cleanly to $[C_{76}{}^+][CB_{11}H_6Br_6{}^-]$.[9] As shown in Figure 1, the oxidation can be followed by vis-near IR spectroscopy using $\lambda_{max} = 780$ nm as the identifying absorption of $C_{76}{}^+$. An identical spectroscopic observation was made with the $SbCl_6{}^-$ salt of the triarylamine oxidant, but the lifetime of $C_{76}{}^+$ in solution was only hours compared to weeks with the carborane counterion. This presumably reflects the greater nucleophilicity of $SbCl_6{}^-$ and possible chloride ion abstraction by $C_{76}{}^+$.

On a preparative scale, C_{76} (10 mg) was treated with a small excess of oxidant in *o*-dichlorobenzene, and after filtration, the product was isolated as a dark brown solid by the addition of hexane (eq 2).

$$\mathrm{C_{76} + [Ar_3N^{\bullet+}][CB_{11}H_6Br_6{}^-] \rightarrow [C_{76}{}^+][CB_{11}H_6Br_6{}^-] + Ar_3N} \tag{2}$$

The triarylamine byproduct was identified in the filtrate by ^1H NMR spectroscopy. Microprobe analysis of the product via Auger electron spectroscopy showed the presence of C, B, and Br (and O, presumably from unavoidable air exposure) and the absence of N (and Ag). At a 10 kV beam voltage, the C/B/Br ratio is 12.5:5.5:1 which, if normalized for anomalously high boron sensitivity using the known B/Br ratio of the carborane anion (1.83:1), indicates an elemental composition ratio of 12.5: 1.83:1 (calcd 12.8:1.83:1).[10] As shown in the top spectrum of Figure 2, the IR spectrum of the isolated product shows sharp absorption bands typical of a well-defined, microcrystalline material. A constituent analysis is provided by the observation that all prominent bands can be assigned to the $CB_{11}H_6Br_6{}^-$ anion (3052, 2600, 1126, 1001, 991, 953, 932, 917, 858, 808, 752, 635, 337, 326 cm^{-1}) or to $C_{76}{}^+$ (1456, 1433, 571, 554, 539, 527 cm^{-1}) plus residual hydrocarbon (2950, 2919, 2850 cm^{-1}). The fullerene cation bands are all within 1−2 cm^{-1} (the resolution limit of the spectrometer) of those of unoxidized C_{76}[11] except for the 1440 cm^{-1} absorption whose frequency has increased in the cation by 16 cm^{-1} to 1456 cm^{-1}.

Consistent with a 1:1 electrolyte, a 3.1×10^{-4} M solution of the product in tetrachloroethane showed $\Lambda_M = 15.0\ \Omega^{-1}\ cm^2\ mol^{-1}$, similar to $[n\text{-}Bu_4N^+][CB_{11}H_6Br_6{}^-]$ ($12.7\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 3.1×10^{-4} M). Dissolution in tetrachloroethane gave a dark brown solution whose ^{11}B NMR spectrum [−1.7 (1B); −9.9 (5B); −20.6, d, $J_{BH} = 160$ Hz (5B)] confirmed the integrity of the anion. In *o*-dichlorobenzene-d_4, the ^{13}C NMR spectrum showed no observable peaks under conditions where C_{76} would have been detectable if present. This is the expected result of paramagnetic line broadening in the $C_{76}{}^{\bullet+}$ radical and leads to

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[9] Reactions were performed in an inert atmosphere glovebox (O_2, H_2O < 1 ppm) in flame-dried glassware. *o*-Dichlorobenzene was purified by distillation, first from CaH_2 and then from Na, and stored over activated alumina. 1,1′,2,2′-Tetrachloroethane was distilled from CaH_2 and stored over alumina. The fullerene C_{76} (99.8%) was purchased from TechnoCarbo.

[10] For compounds of known composition containing the $CB_{11}H_6Br_6{}^-$ ion (and no other B or Br), the B/Br ratio at 10 kV (required for Br sensitivity) is always high and varies with composition (e.g., for $[Bu_4N^+][CB_{11}H_6Br_6{}^-]$: found 7.6:1; calcd 1.83:1.

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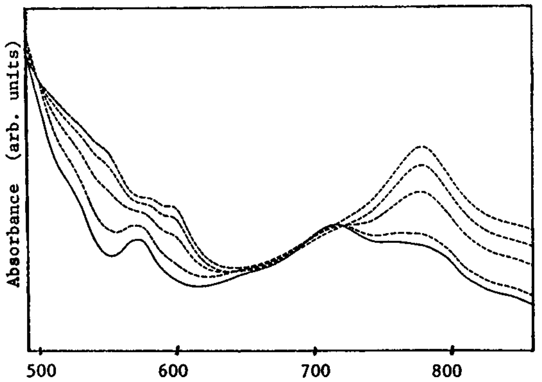

Figure 1. Progressive spectrophotometric (nm) oxidation of C_{76} (solid line) with $[Ar_3N^{\bullet+}][CB_{11}H_6Br_6^-]$ in 1,1′,2,2′-tetrachloroethane to form C_{76}^+. Excess oxidant causes no further change in bands ascribable to C_{76}^+.

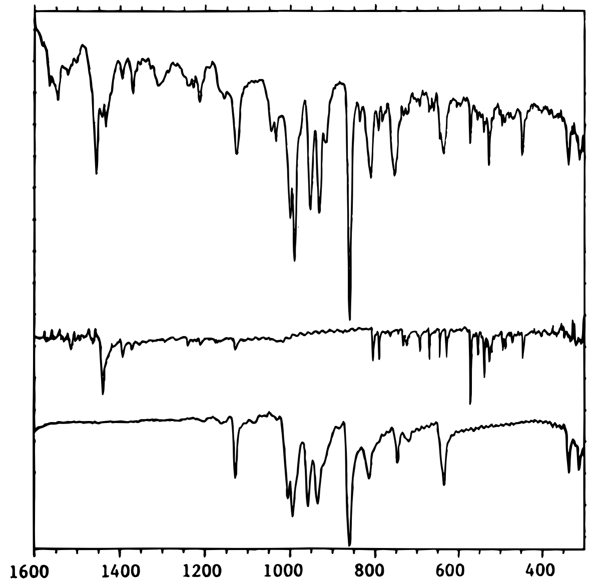

Figure 2. FTIR (KBr) spectrum (cm^{-1}) of $[C_{76}^+][CB_{11}H_6Br_6^-]$ (top) in the fullerene region, C_{76} (middle), and $Cs(CB_{11}H_6Br_6)$ (bottom). The complete spectra are available as Supporting Information.

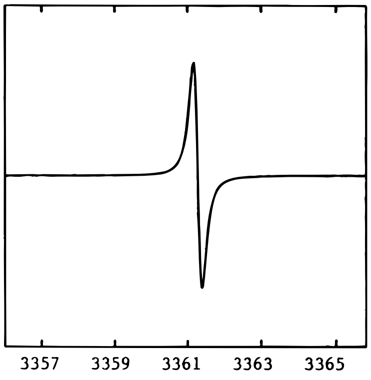

Figure 3. EPR spectrum (G) of the C_{76}^+ radical in frozen *o*-dichlorobenzene as $CB_{11}H_6Br_6^-$ (150 K, 20 μW, 0.02 G mod).

the reciprocal expectation of a sharp, readily observable EPR spectrum. As shown in Figure 3, this expectation is borne out. An isotropic doublet is observed in frozen o-dichlorobenzene solution with $g = 2.0030$, very close to the free electron value, and a narrow line width of 0.5 G with little temperature dependence. This signal is readily observed even in the presence of excess oxidant ($\Delta H = 37$ G) because of the 70-fold difference in line width. In the solid state, the *g* value of the isolated product is 2.0042 and $\Delta H = 2.7$ G. These EPR characteristics are similar to those believed to be associated with C_{60}^{+}.[2b,f] A further distinctive feature of C_{76}^+ is expected to be an abundance of low-energy absorption bands in its electronic spectrum. A series of closely spaced highest occupied molecular orbitals have been calculated for C_{76}[12] such that an electron hole in the HOMO should give rise to numerous transitions with near IR energies. As shown in Figure 4, several bands are in fact observed for C_{76}^+ (λ_{max} (nm) = 780, 830 sh, 980, 1040 sh); C_{76} has no maxima greater than ca. 850 nm (see Figure 1).

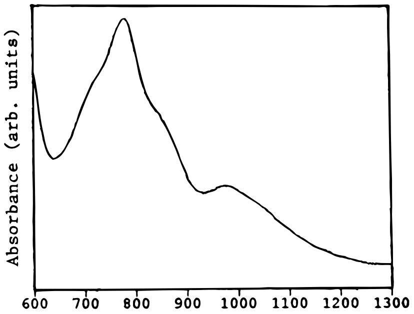

Figure 4. Near IR spectrum (nm) of C_{76}^+ in 1,1′,2,2′-tetrachloroethane.

The chemical reactivity of C_{76}^+ is expected to be that of (a) a strong one-electron oxidant and (b) a substrate for nucleophilic addition. The former can be readily demonstrated by vis-near IR reduction back to C_{76} with iodide ion (1.05 ± 0.06 equiv of $Bu_4N^+I^-$) and by oxidation of 9,10-diphenylanthracene ($E° = 0.8$ V)[13] to its distinctive radical cation (λ_{max} (nm) = 595, 661, 750).[14] Non-oxidizable nucleophiles (Nu^-) are expected to react with fullerene cations according to eq 3, but the price and availability of C_{76}[15] presently discourage exploration of this potentially useful functionalization route.

$$2\text{fullerene}^+ + 2\text{Nu}^- \rightarrow \text{fullerene(Nu)}_2 + \text{fullerene} \quad (3)$$

In summary, a new "electron hole" oxidant, $[Ar_3N^{\bullet+}][CB_{11}H_6Br_6^-]$, allows the synthesis and isolation of a salt of a fullerene cation, C_{76}^+. This is the first fullerene cation to be isolated and well characterized and, to the best of our knowledge, is the first example of an all-carbon carbocation. Continued reagent development should lead to the synthesis of other desirable cations (e.g., C_{60}^+) and open the way to controllable reactivity with trapping nucleophiles,[16] to mechanistic studies, and to potential material science applications involving spheroidal radical cations.

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Supporting Information Available: Full spectral range IR of $[C_{76}^+][CB_{11}H_6Br_6^-]$ (1 page). See any current masthead page for ordering and Internet access instructions.

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[15] Fullerene C_{76} is commercially available in milligram quantities at ca. $40 000 per gram.

[16] Multiple additions of nucleophiles to C_{60} to give mixtures of C_{60}-Nu_{2x} products have been reported under oxidative conditions. For example, see: (a) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9385−9387, 9387−9388. (b) Chiang, L. Y.; Upasani, R. B.; Swirczewski, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 10154−10157. (c) Miller, G. P.; Buretea, M. A.; Bernardo, M. M.; Hsu, C. S.; Fang, H. L. *J. Chem. Soc., Chem. Commun.* **1994**, 1549−1550. (d) Lem, G.; Schuster, D. I.; Courtney, S. H.; Lu, Q.; Wilson, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 554−555. Multiple halogen additions to C_{60} are also well established.[1]