

Condensation Products from the Anionic Radicals of C₆₀ and the Common Solvent: Hexamethylphosphoramide

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Both freshly sublimed C₆₀ and “off-the-shelf” C₆₀ were reduced with the alkali metals in hexamethylphosphoramide (HMPA). When pure C₆₀ is reduced to its trianion radical, it condenses with a molecule of HMPA to yield C₆₀^{3−}(HMPA)[•], which exhibits a typical EPR pattern for a system with a doublet multiplicity and hyperfine splitting from the ³¹P (*a*_{31P} = 0.93 G). When Rb or Cs serves as the reducing metal, hyperfine is observed from the metal cation (*a*_{133Cs} = 0.78 G, *a*_{87Rb} = 1.393 G), which is involved in tight ion association with the P=O moiety (C₆₀^{3−}(HMPA)[•]M⁺). The small cations do not form intimate ion pairs, and both C₆₀^{3−}(HMPA)[•] and C₆₀^{3−}(HMPA)₂[•] are present in solution when M = Na or Li. The latter species exhibits an EPR splitting from two ³¹Ps. The “off-the-shelf” C₆₀ contains C₁₂₀O as an impurity. Extensive reduction of this impurity results in a charged multianionic state where very large splittings from three ³¹Ps are observed.

The anions of C₆₀ have come to be intensively investigated because of their unique electronic and magnetic properties and in part because of their ease of formation. For example, K₃C₆₀ has been shown to act as a superconductor at 18 K,¹ and the anion radical (yielding a single EPR resonance)² of C₆₀ is a semiconductor.^{1b} Also, C₆₀ is known to have a very large solution electron affinity³ because of its low-lying triply degenerate t_{1u} LUMO (Figure 1),⁴ which accepts up to six electrons, producing a stable hexa-anion.⁵ Despite their thermodynamic stabilities, the anions of C₆₀ are very reactive,⁶ as is the neutral C₆₀ molecule.⁷

In a preliminary communication,⁶ we reported that the cesium salts of cyclooctatetraene-C₆₀ complexes spontaneously react with one of the most common solvents for anions, hexamethylphosphoramide (HMPA). HMPA is one of the most powerful solvating agents for cations, and it totally prevents ion association between hydrocarbon anions and metal cations.^{8,9a} The Gutmann donor number for this nonprotic solvent is 38.8 (that for water is 18.0).^{9b} This number is sufficiently high to allow HMPA to support the solvated electron in the presence of all of the alkali metals. EPR investigations of anion radicals in HMPA do not reveal metal hyperfine splittings, unless the anion radical is highly polar, e.g., the nitrobenzene anion radical.⁸

The paramagnetic products obtained from the Cs metal reduction of a mixture of cyclooctatetraene and C₆₀ yield EPR spectra that clearly exhibit signals from the phosphorus atom in the solvent as well as from the cesium cation.⁶ We initially thought that the ¹³³Cs hyperfine (*a*_{133Cs}) originated from an endohedral cation.^{6,10} However, we later realized that the HMPA reacts with the resulting radical ion(s) to produce a paramagnetic product that is in turn ion associated with ¹³³Cs⁺.¹¹

The ambient temperature solution EPR spectra of C₆₀^{•−} and C₆₀^{3−} in a wide variety of solvents (not including HMPA) appear as single broad lines.¹² The line width is large because of the shortening of T₁ from dynamic averaging over thermally accessible excited states.¹² However, when the C₆₀ is substituted, the symmetry is lowered and the degeneracy of the LUMO is

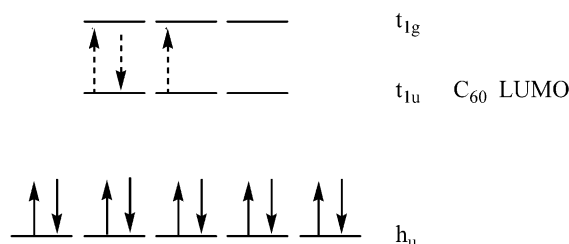
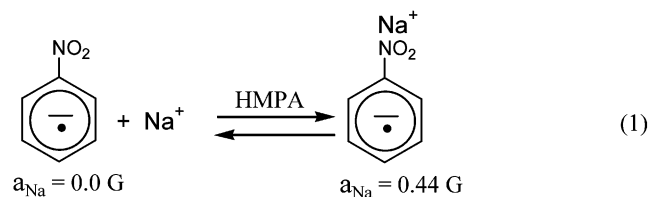


Figure 1. Molecular orbitals diagram depicting the HOMO, LUMO, and LUMO+1 molecular orbitals of C₆₀ reduced to the −3 state. The dashed arrows represent the added electrons that go into the LUMO.

broken, leading to sharper EPR transitions.¹² It is important to note that C₆₀^{2−} and C₆₀^{4−} exist as EPR silent singlet states.¹³

As mentioned above, ion association in HMPA is rare and only takes place when the anion is very polar or multiply charged.^{8,9a} The free solvated anion radical of nitrobenzene in HMPA in the presence of Na⁺ is in equilibrium with the ion associated species (reaction 1), for which *a*_{23Na} is 0.44 G at ambient temperatures.^{8a} When the C₆₀^{n−} system becomes



attached to a polar P=O moiety, ion association is also possible in HMPA. Here we report a series of reactions of the salts of C₆₀ with HMPA to form a family of phosphorus-containing products that yield highly resolved EPR spectra reflecting their structures and ion pairing properties. Well after this work was initiated, it became clear that all EPR work carried out on the anions of C₆₀ is particularly susceptible to error caused by the C₁₂₀O impurity, which has a higher solution electron affinity than does C₆₀.^{13,14} To quote a recent statement by Reed and co-workers,¹³ “...with the exception of C₆₀ samples freshly

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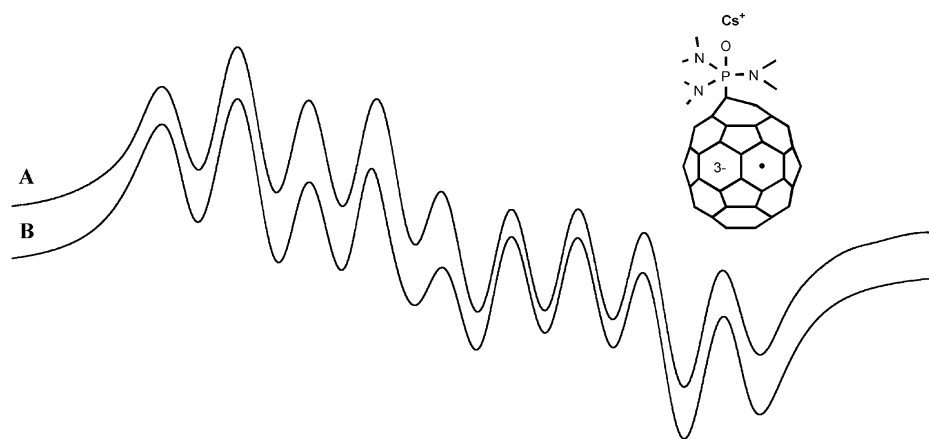


Figure 2. (A) 10 G EPR spectrum of C_{60}^{3-} -HMPA* obtained after the addition of ca. 3 equiv of Cs metal to the same solution. (B) A computer simulation generated using a single ^{133}Cs splitting of 0.725 G, a ^{31}P splitting of 0.93 G, and a line width of 0.55 G. A small contribution (4%, slightly shifted downfield) from residual paramagnetic C_{60}^{n-} species is included.

prepared by vacuum sublimation, $C_{120}\text{O}$ has been an unrecognized small but ubiquitous impurity in nearly every physical measurement ever made on C_{60}^{n-} . As a consequence of this statement, our EPR experiments were repeated with the use of freshly sublimed C_{60} , which was not allowed to come into contact with air at any time during the experiment. Indeed, these later experiments led to significantly altered results.

Results and Discussion

When C_{60} is mixed with dry HMPA, under high vacuum conditions, the resulting mixture is heterogeneous (C_{60} is insoluble in HMPA) and yields a short-lived weak signal upon EPR analysis. The dominant feature in the EPR spectrum is a single broad resonance ($\Delta w_{\text{pp}} = 0.7$ G). Clearly, there is a small degree of electron transfer that takes place from the HMPA to the C_{60} . This is not unexpected, as C_{60} acts as the acceptor in an electron-transfer process with a variety of amines.¹⁵

The initial reduction of this heterogeneous mixture with any of the alkali metals immediately gives rise to the strong EPR signal for C_{60}^{n-} . The signal consists of a single resonance with a peak-to-peak line width (Δw_{pp}) of about 0.9 G. This signal is clearly due to the monoanion radical, with the ubiquitous $C_{120}\text{O}^{n-}$ impurity.¹³ The lack of a signal with a narrow line width indicates the absence of a substituted C_{60}^{n-} monomer.

After the further addition of more than two equivalents of cesium, rubidium, or potassium, small satellite signals, two on each side of the intense central signals for C_{60}^{n-} , appear (see Figure 2 in ref 6). These satellite signals originate from a doublet species, in which one unpaired electron is coupled with three spin $1/2$ nuclei. These spectra are unchanged when the reduction is carried out in per-deuterated HMPA. Hence, the spin $1/2$ satellites are due to phosphorus splittings, as ^{31}P is the only $I = 1/2$ nucleus present in the sample.

In each case, two of the phosphorus nuclei are identical with $a^{31}\text{P} \approx 12.5$ G, but the third phosphorus has a slightly larger spin density ($a^{31}\text{P} \approx 13.5$ –14 G). When either Cs or Rb serves as the reducing agent further splittings of the ^{31}P satellites because of the alkali metal cations are observed. The nuclear spin for ^{133}Cs is $7/2$, and the ^{31}P satellites are further split into 8 hyperfine components with $a^{133}\text{Cs}$ equal to 0.78 G. An analogous splitting of the ^{31}P satellites from both isotopes ($I = 5/2$ for ^{87}Rb and $I = 3/2$ for ^{85}Rb) is observed in the rubidium system. On the other hand, no alkali metal splitting of the ^{31}P satellites can be seen when K^+ serves as the counterion. A likely explanation is the very low gyromagnetic ratio of ^{39}K .

When the C_{60} is sublimed directly into the evacuated reduction chamber, the ^{31}P satellite signals cannot be observed. The ^{31}P satellite signals appear to originate from the $C_{120}\text{O}$ impurity. It seems reasonable that the signal originates from $C_{120}\text{O}^{n-}$ which has condensed with three HMPA molecules. At least one of the $\text{P}=\text{O}$ groups is strongly ion associated with the alkali metal cation.

Because the ^{31}P satellites are not observed early in the reduction, when $C_{120}\text{O}^{n-}$ and C_{60}^{n-} are present, the species giving rise to these satellites is not a condensation product involving $C_{120}\text{O}^{n-}$. Consequently, this species must originate from a multiply charged $C_{120}\text{O}$ that has probably fragmented and condensed with three HMPA molecules. It should be noted here that no analogous signal is observed when either Na or Li serves as the reducing agent. Hence, the formation of this species is very dependent upon ion association conditions.

The addition of more alkali metal to the solution results in the disappearance of the impurity signal. After more than four mole of Cs per mole of C_{60} are added, the spectrum evolves into an octet from an $I = 7/2$ cesium nucleus ($a^{133}\text{Cs} = 0.725$ G), which is further split by a single ^{31}P nucleus with $a^{31}\text{P} = 0.93$ G, Figure 2. The very broad line width (0.55 G) is partially attributed to the unresolved splittings from the carbon-13 nuclei. There are 60 (many nonequivalent) carbons that are in proximity to the Cs^+ . The species giving rise to this EPR spectrum is $C_{60}^{3-}(\text{HMPA})^*\text{Cs}^+$ where the fullerene contains three extra (added) electrons. This final doublet species is invariant whether “off-the-shelf and unsublimed” or freshly sublimed C_{60} is used. Further reduction of this species with Cs metal results in the loss of the EPR signal because of the formation of the diamagnetic tetra-anion of C_{60} . The $C_{60}^{3-}(\text{HMPA})^*\text{Cs}^+$ solutions remain EPR silent even after more than a fifth equivalent of metal is added. Apparently, the penta-anion disproportionates to the tetra- and hexa-anions.

Analogously, the nearly exhaustive reduction of C_{60} in HMPA with Rb results in the formation of two doublet species, each exhibiting hyperfine splitting from a single ^{31}P ($a^{31}\text{P} = 1.0$ G). The two species arise from the two isotopes of Rb ($I^{87}\text{Rb} = 3/2$, and $I^{85}\text{Rb} = 5/2$). The dominant species (72%) exhibits $a^{85}\text{Rb} = 0.411$ G [$C_{60}^{3-}(\text{HMPA})^*,^{85}\text{Rb}^+$]. The other species shows an $a^{87}\text{Rb}$ of 1.393 G [$C_{60}^{3-}(\text{HMPA})^*,^{87}\text{Rb}^+$], Figure 3. The PM3 prediction of the structure of $C_{60}^{3-}(\text{HMPA})^*\text{Li}^+$ (the PM3 protocol is not compatible with metals larger than Li) is shown in Figure 4.

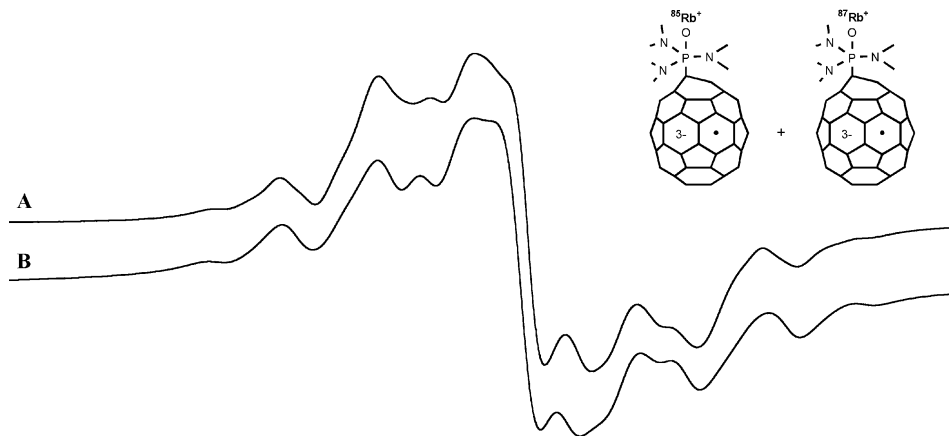


Figure 3. (A) 10.5 G EPR spectrum of C₆₀³⁻-HMPA* obtained after the addition of ca. 3 equiv of Rb metal to the same solution. (B) A computer simulation generated using a Rb splitting of 0.411 G for ⁸⁵Rb and 1.393 G for ⁸⁷Rb (natural abundance ratio), a ³¹P splitting of 1.0 G, and a line width of 0.45 G. Contributions from residual paramagnetic C₆₀ⁿ⁻ species are included.

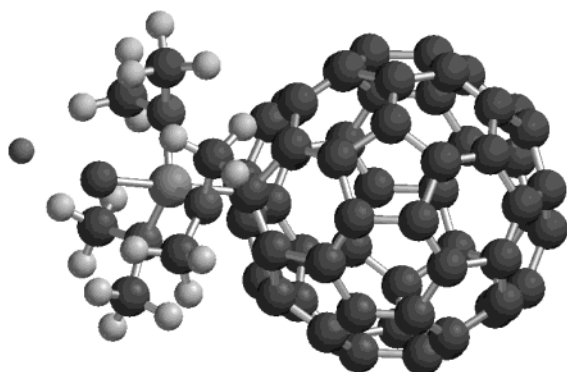


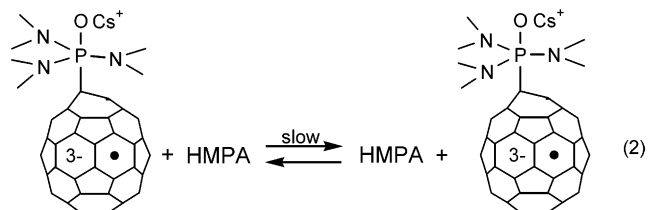
Figure 4. PM3 predicted structure for C₆₀³⁻(HMPA)*, M⁺ where M = Li. The calculated spin density at the ³¹P nucleus is quite large ($|ρ^{31P}| = 0.048$). The EPR spectra for this species where M = Cs and Rb are shown in Figures 2 and 3, respectively.

The dynamics of the C₆₀ reductions are very different when the smaller alkali metals serve as the source of electrons. The reduction of C₆₀ with sodium metal in HMPA first yields, as expected, the single resonance for C₆₀^{•-}. This broad single resonance is the only observable signal present until nearly three mol of Na per mol of C₆₀ have been added. At this point, the single resonance is replaced by a six line EPR pattern, which is a result of the presence of two different ion radicals. One of these radicals yields a doublet of doublets due to two single nonequivalent (³¹P) spin 1/2 nuclei with $a^{31P} = 2.13$ and 1.80 G. The other radical yields a doublet from a single phosphorus nuclei, $a^{31P} = 1.95$ G, Figure 5.

Lithium reductions yield EPR spectra that can be simulated with the same parameters, and identical results are obtained when the reduction is carried out with either ⁶Li or ⁷Li. Clearly, these species do not yield metal hyperfine splittings. The weaker ion association is due to the better solvation of the smaller cations by the HMPA solvent system.¹⁶ The Li and Na systems yielding the hyperfine splitting from the single ³¹P are analogous to those obtained in the C₆₀³⁻(HMPA)*,Cs⁺ and C₆₀³⁻(HMPA)*,Rb⁺ systems but without the tight ion association (structures I and II) and consequent metal hyperfine. The other species present, represented by the doublet of doublets, clearly has two ³¹P=O groups attached to the C₆₀. In the absence of intimate ion association, C₆₀³⁻ “prefers” to be associated to one or two HMPA units. When tight ion association is present (the larger cations) only a single HMPA is attached to the C₆₀³⁻ unit, and cesium or rubidium hyperfine is present.

The rate of formation and dissociation of the C₆₀³⁻-HMPA bond is slow on the EPR time scale. However, this bond is very weak and tenuous, as evidenced by the addition and removal of HMPA molecules with variations in the degree of ion association. The addition of water to the HMPA solutions containing the C₆₀³⁻(HMPA)*,Cs⁺ complex yields a brown intractable material. The solids were collected via filtration and were extracted with toluene for 24 h in a Soxhlet. Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy of the water quenched solution reveals peaks at each mass to charge unit from 720 to 727. These represent the parent (P) and P + 1 peaks of the Birch reduction products of the anions of C₆₀. No heavier materials were found, and in no case was there evidence of a mass-to-charge ratio consistent with one or more HMPA molecules attached to a C₆₀. Evidently, work up and isolation results in the loss of the tenuously attached HMPA. The HMPA condensation products represent transient species, which cannot be isolated for X-ray or other studies, and the regiochemistry of II is unknown.

To see if the C₆₀³⁻-HMPA bond formation and dissociation is fast on the NMR time scale, solutions of C₆₀³⁻-HMPA were generated in HMPA via Cs reduction, and their ³¹P NMR spectra were recorded on a 300 MHz (¹H) spectrometer. The presence of the C₆₀³⁻(HMPA)*,Cs⁺ resulted in considerable broadening of the WALTZ ¹H decoupled ³¹P NMR resonance. The full width of the central line is roughly 10 Hz, but the nine hyperfine lines due to the three ¹⁴N nuclei are still resolved. In fact, the degree of line broadening is no different from that observed for the same concentration of the naphthalene anion radical dissolved in HMPA. Hence, reaction 2 proceeds but is slow on the EPR and NMR (observation of solvent) time scales.



Conclusions

Freshly sublimed C₆₀ can be reduced to its trianion radical in HMPA with any of the alkali metals. The resulting trianion radical condenses with HMPA molecule(s). The HMPA-C₆₀ complex forms tight ion pairs with Rb⁺ or Cs⁺, and the final

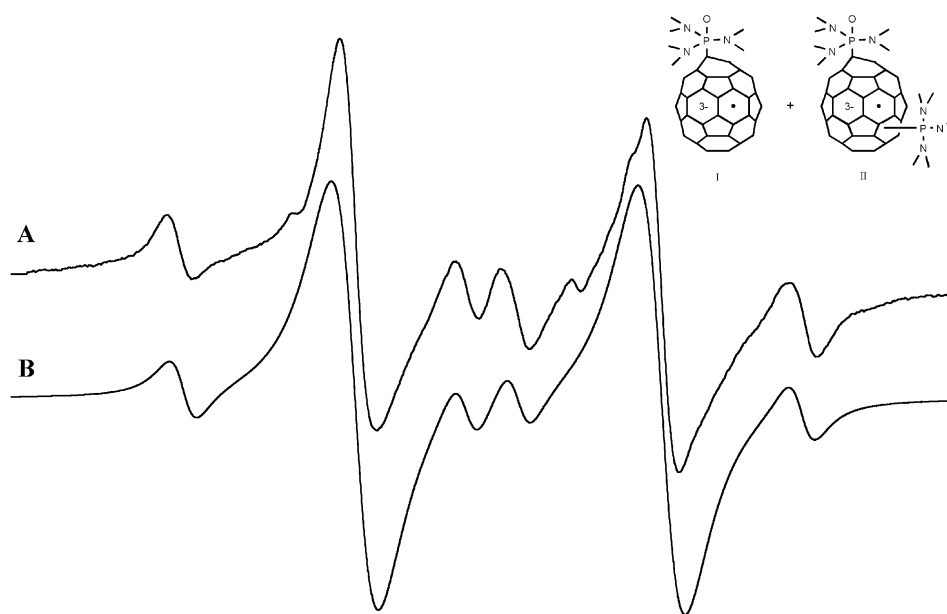


Figure 5. (A) 6 G EPR spectrum of the trianion radical of C_{60} in HMPA when sodium serves as the reducing agent. The species responsible for the signal are assigned to $C_{60}^{3-}(\text{HMPA})^{\bullet}\text{Na}^{+}$ and $C_{60}^{3-}(\text{HMPA})_2^{\bullet}\text{Na}^{+}$ (B) computer simulation of a mixture of species using the coupling constants of $a^{31\text{P}} = 1.95$ G for one ^{31}P species and $a^{31\text{P}} = 2.13$ and 1.80 G for a second ^{31}P species. The peak-to-peak line widths are 0.3 and 0.18 G, respectively, and their relative concentrations are 10:1, structure I:structure II.

$C_{60}^{3-}(\text{HMPA})^{\bullet}\text{M}^{+}$ species is kinetically stable and yields metal hyperfine upon EPR analysis. Tight ion pairing does not take place with Li^{+} or Na^{+} , and the $C_{60}^{3-}(\text{HMPA})^{\bullet}$ can condense with one more HMPA unit. Hence, when the smaller alkali metals serve as the reducing agent, both $C_{60}^{3-}(\text{HMPA})^{\bullet}$ and $C_{60}^{3-}(\text{HMPA})_2^{\bullet}$ are found in the HMPA solutions.

If the common impurity $C_{120}\text{O}$ is present, potassium, rubidium, or cesium reduction results in a solution exhibiting an EPR signal from an ion pair with a very large $a^{31\text{P}}$. The striking difference between the EPR spectra of $C_{60}^{3-}(\text{HMPA})^{\bullet}\text{M}^{+}$ and the radical originating from C_{120}^{n-} is the magnitude of the ^{31}P hyperfine splitting, averaging 13 G in the latter and less than 2 G in the former. PM3 calculations carried out on the anions of $C_{120}\text{O}^{n-}(\text{HMPA})_3^{\bullet}$ yield no encouragement concerning the existence of such a species with high spin densities on the phosphorus nuclei. The species giving rise to the splitting from three ^{31}P s with large couplings must contain a C_{60} or $C_{60}\text{O}$ anionic radical fragment of $C_{120}\text{O}^{n-}$. Krusic and co-workers have observed very large carbon spin densities on the *tert*-butyl- C_{60} radicals produced via the cleavage of the *tert*-butyl- C_{60} - C_{60} -*tert*-butyl dimer.¹⁷ Their radical (*tert*-butyl- C_{60}^{\bullet}) is neutral, however, and the one giving rise to the ca. 13 G splitting is multiply charged (ion associated in HMPA) and substituted with three HMPA units. We have been unable to find a reasonable structure that accommodates these requirements, but, whatever it is, it is an impurity caused by $C_{120}\text{O}$.

Experimental Section

All reductions were carried out in sealed Pyrex glass apparatuses under high vacuum, Figure 6. The C_{60} was sublimed from tube A into bulb B of the apparatus. Tube A, containing some residual C_{60} and $C_{120}\text{O}$ impurities, was subsequently sealed from the apparatus. The HMPA was then distilled directly into the evacuated apparatus through joint C from a potassium/HMPA solution. The alkali metals, with the exception of Li, were sublimed into bulb D to form metal mirrors. After the apparatus was sealed from the high vacuum line at point E, the HMPA mixtures in bulb B were exposed for various amounts

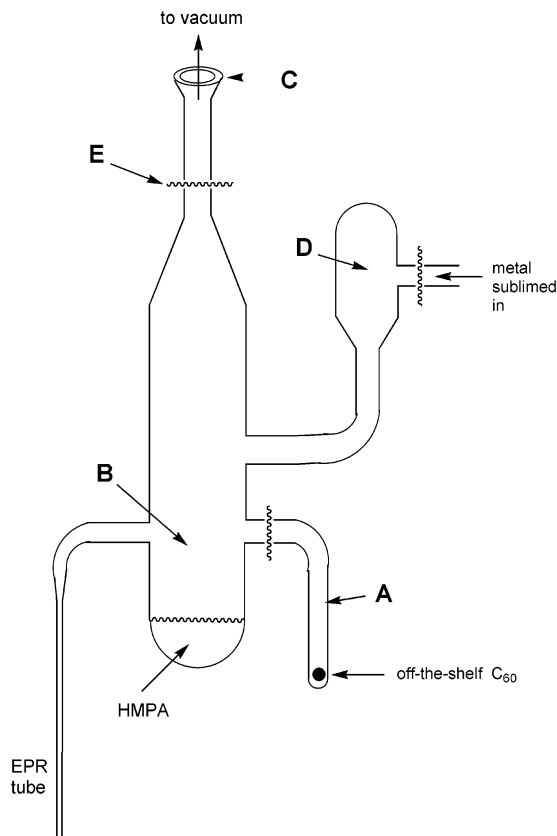


Figure 6. All Pyrex glass apparatus used for the alkali metal reductions of the HMPA-fullerene mixtures.

of time to the freshly distilled metal mirrors by inverting the apparatus. In the case of lithium, which is very difficult to sublime in Pyrex glass, a freshly cut piece of metal was placed directly into the bulb D. In experiments using "off-the-shelf" C_{60} (99.5% from Aldrich Chemical Co.), the C_{60} was simply placed in the bottom of bulb B prior to attachment to the vacuum line.

X-band EPR data were obtained using a Bruker EMX spectrometer operating at 9.77 GHz with a standard rectangular cavity; modulation frequency, 100 kHz; modulation amplitude, 0.1 G. Computer simulations of the experimental EPR spectra were carried out using EWSim, version 4.0, from Scientific Software Services, Normal, IL.

Full geometry optimization calculations on the C₆₀ complex were carried out using the PM3 protocol and TITAN (Jaguar 3.5, Schrödinger, Inc., Portland, Oregon, 1998).

Several samples were reduced in the apparatus shown in Figure 6 to the point where the EPR spectrum for C₆₀³⁻(HMPA)⁺, M⁺ shown in Figure 2 was evident. The tube (D) containing the excess metal was then removed, and the samples were quenched with DI water. The water solutions were titrated with standardized HCl solutions. This procedure was used to find the number of cesium atoms per C₆₀ molecule in the original HMPA solutions.

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