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A Novel Synthetic Route for the Formation of the Biphenyl Anion from Benzene Using Fullerene Anions

Michael P. Eastman,* Carrie L. Wyse, John P. Abe, and Robert W. Zoellner

Department of Chemistry, Northern Arizona University, Flagstaff, Arizona 86011-5698

Robert G. Kooser

Department of Chemistry, Knox College, Galesburg, Illinois 61401-4999

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The electrochemical and chemical reduction of C_{60} is of current interest because of the discovery of superconducting alkali metal-doped C_{60} phases and the value of C_{60} in chemical syntheses to form new compounds of interest to chemistry and materials science. Recent work[1] has led to the characterization of several of the reduced states of C_{60} through the use of electrochemical and spectroscopic methods and forms the basis for new uses of C_{60} as a synthetic tool in chemistry. Here we report that 18-crown-6 (18C6)-assisted potassium metal reduction of C_{60} in benzene at room temperature leads to the coupling of benzene and ultimately the formation of the biphenyl anion.

In the past, we reported the formation, in benzene, of ionophore complexed alkali metal tight ion pairs of the durosemiquinone anion.[2] In initiating the work reported here, we were originally interested in forming ion pairs involving C_{60} and observing the effects of tight ion pairing on the triply degenerate levels occupied by the added electrons. Our experiments involved allowing dilute (5×10^{-4} M) benzene solutions of C_{60} to come in contact with an alkali metal mirror in the presence of crown ethers. The reduction potential in these experiments is controlled by the alkali metal and, to a lesser extent, the ionophore.[3] Here, experiments exploring the potassium reduction of C_{60} in the presence of 18C6 are described. It is known that potassium in the presence of 18C6 can reduce benzene to the benzene anion radical.[4] Thus, it is reasonable to believe that in systems with benzene as a solvent, potassium and 18C6 can reduce C_{60} to various anionic states; this is because C_{60} is more readily reduced than benzene.[1,5]

Results and Discussion

Using a potassium mirror and a 1:1 ratio of 18C6 to C_{60} under vacuum in benzene, a finely divided solid precipitate rapidly forms. The precipitate yields a single ESR line with a g value of 2.0029 and a line width of 0.18 mT; the spectrum is temperature independent between 150 and 300 K. Similar signals under extreme reducing conditions have been previously observed.[6] Increasing the 18C6−C_{60} ratio to 2:1 produces a solid that does not yield an ESR signal at room temperature. When the 18C6−C_{60} ratio is increased to 3:1, a paramagnetic species is produced that gives the spectrum in Figure 1. The reaction time for the formation of the free radical is generally a few minutes. Once formed, the radical is stable, under vacuum, for a period of months. If deuterated benzene is used as the solvent, the ESR spectrum obtained is that given in Figure 2; this demonstrates that the species producing the spectra in Figures 1 and 2 is derived from the solvent and not from an impurity in C_{60} or some other source.

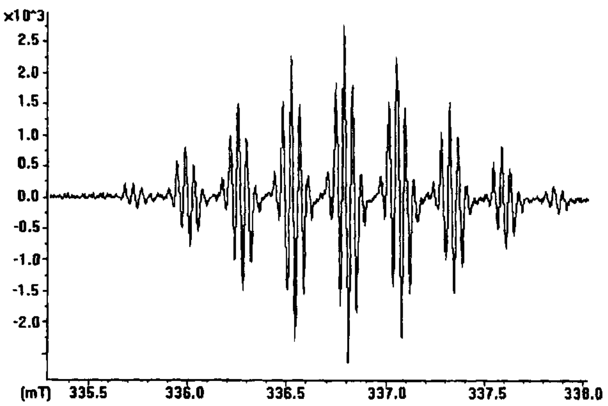

Figure 1. Room temperature ESR spectrum of a 3:1 18-crown-6:C_{60} solution in benzene after being placed in contact with a potassium mirror; the spectrum is that of the biphenyl anion. The ordinate is in millitesla (mT); the modulation amplitude was 4 x10^{-4} mT and the microwave attenuation 35 dB at 9.45576 GHz.

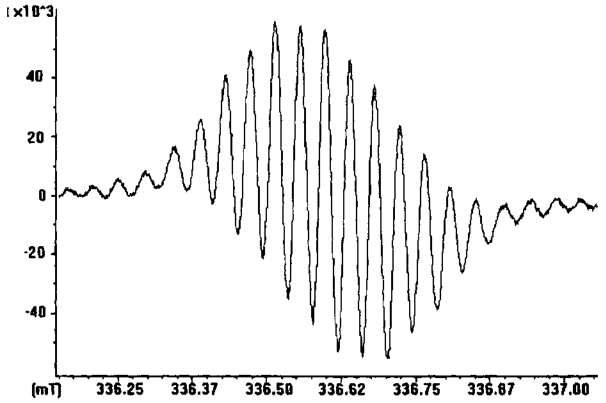

Figure 2. Room temperature ESR spectrum of a 3:1 18-crown-6:C_{60} solution in benzene-d_6 after being placed in contact with a potassium mirror; the spectrum is that of the perdeuteriobiphenyl anion. The ordinate is in millitesla (mT); the modulation amplitude was 5.7 x10^{-4} mT and the microwave attenuation 35 dB at 9.45187 GHz.

The spectrum displayed in Figure 1 was simulated by using two sets of four protons (splitting 0.041 mT and 0.266 mT) and one set of two protons (splitting 0.532 mT) with a line width of 0.022 mT and provides an almost identical match to the experimental spectrum in Figure 1. The splittings used in the simulation are nearly identical to those reported for the biphenyl anion in a

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variety of other systems.[7] Simulations for the deuterated benzene case in Figure 2, using the proton coupling constants above that were adjusted for the difference in gyromagnetic moment of the nuclei, gave a close match to the experimental spectrum in Figure 2. The results of our experiments on C_{60} led to an experiment in which biphenyl dissolved in benzene (5×10^{-4} M) was reduced on a potassium mirror in the presence of an equimolar concentration of 18C6. The spectrum obtained was identical to that in Figure 1 with both yielding a g of 2.0028. Optical spectra taken on the two samples using a diode array spectrophotometer showed both systems exhibited strong peaks of similar shape centered at 420 nm. Attempts to produce similar results with C_{60} using sodium as the reductant and either 18C6 or 15-crown-5 as the ionophore produced only the material observed in the 1:1 potassium case.

A possible rationale for the reaction we observed is the following:

$$3K + 3(18C6) + C_{60} \rightarrow (C_{60})^{3-} + 3(K^+\ 18C6) \quad (1)$$

$$(C_{60})^{3-} + 2C_6H_6 \rightarrow (C_{60}H_2)^{2-} + (C_{12}H_{10})^- \quad (2)$$

Here we have not explicitly shown the ion pairing that almost certainly occurs between the ions and the crown-complexed potassium. Spin concentration measurements using a nitroxide standard show that the yield of our reaction is approximately 30% based on the amount of C_{60} initially present. The species $C_{60}H_2$ is well known;[8] $C_{60}H_2^-$ and $C_{60}H_2^{2-}$ have been generated electrochemically.[9] Evidence for the existence of $C_{60}H_2^{2-}$ in our system is somewhat circumstantial. In the early stages of one of our 3:1 reduction experiments, a transient paramagnetic species appeared with a three-line ESR spectrum (1:2:1 intensity ratio, $g = 2.002$ and 0.32 mT splittings). This signal could be observed at microwave powers sufficient to saturate the signal from the biphenyl anion radical. The ESR spectrum previously reported for $C_{60}H_2^-$ was taken at 160 K in toluene and consisted of a single 0.3 mT line centered at $g = 2.000$.[9]

Graphite intercalation compounds of potassium and rubidium such as KC_{24} are known to cause the polymerization of benzene to biphenyl , terphenyl, and quaterphenyl.[10] This reaction, when carried out with potassium, forms detectable amounts of biphenyl in about 1 day at room temperature and is capable of producing terphenyl and quaterphenyl when the reactants are heated. It is also known that C_{60}, by itself, facilitates the coupling of aromatics in coal liquification reactions.[11] Thus, the coupling reaction reported here is noteworthy because it demonstrates the reactivity of C_{60}^{3-}; it takes place relatively rapidly at room temperature and it produces only the biphenyl radical. Here the coupling reaction is carried out in a system with a K:C ratio of 1:20 while for the system employing the graphite intercalation compounds the ratio is 1:24.

The work described here is of significance for ESR spectroscopists because it allows, according to the "rationale" presented, the preparation of the biphenyl free radical in the absence of unreduced biphenyl. In general, line width and relaxation time measurements for an anion radical can be significantly affected by the presence of unreduced parent molecule.[12] Furthermore, because of the reactivity of C_{60}^{3-}, considerable care must be given to assigning the ESR spectra observed in systems nominally designed to produce the C_{60}^{3-} radical. This point has been discussed by Eaton and co-workers in systems where the evidence for reactivity was convincing but the exact nature of the products uncertain.[1]

Experimental Section

The C_{60} and 18C6 were obtained from Aldrich Chemical and were used as received. A.C.S. spectrophotometric grade benzene was obtained from Aldrich and benzene-d_6 (99.6 atom % deuterium) from Isotec Inc.; both were dried over sodium and under vacuum prior to the preparation of the samples. The ESR samples were prepared under high vacuum in tubes having an alkali metal mirror separated by a break seal from the benzene solution of C_{60} and 18C6. The preparation of the samples involved fracturing the break seal and bringing the benzene solution in contact with the mirror. Periodically the sample was removed from the mirror and transferred to the side arm attached to the sample tube (a 4 mm o.d. quartz ESR tube from Wilmad Glass Co. Inc.) and the ESR or optical spectrum of the sample recorded. This process was repeated until there was no further change in the spectral properties of the solution.

ESR spectra were taken on a Bruker ESP-300E x-band spectrometer equipped with a Bruker temperature controller and a Hewlett-Packard 5350 B microwave frequency counter. The standard for the g value measurements was 2,2-diphenyl-1-picrylhydrazyl ($g = 2.0037$). Optical experiments were carried out using a Hewlett-Packard Model 8452 A diode array spectrometer; in these experiments the ESR side arm of the sample tube was placed in the spectrometer beam and the spectrum recorded.

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