Chem. Mater. **1997,** *9,* 3049−3051

Preparation of Rb_3C_{60} Utilizing Room-Temperature Solubilization in Alkylamines

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Received May 28, 1997. Revised Manuscript Received July 30, 1997[⊗]

Alkylamines (*n*-propylamine and *n*-butylamine) can be employed at room temperature as solvents for the preparation of alkali-metal-intercalated C_{60}. In this work, the preparation of Rb_3C_{60} was studied in detail. The reaction produces a single phase as characterized by X-ray diffraction structural analysis. The product shows a superconducting transition at $T_c \sim 28$ K after thermal elimination of the amine. A stepwise mechanism of intercalation is proposed in which a fullerene−amine adduct forms first, followed by charge transfer between the adduct and Rb metal, followed by thermal decomposition of the adduct to yield Rb_3C_{60}.

Introduction

Superconducting fullerides M_3C_{60} (M = K, Rb, and various mixtures of alkali atoms) have attracted great interest since the discovery of superconductivity below 18 K in potassium-intercalated fullerene C_{60} in 1991.[1] The superconducting transition temperature (T_c) is found to increase with lattice expansion of the face-centered cubic (fcc) unit cell of a M_3C_{60} phase,[2] in which alkali-metal ions occupy both octahedral and tetrahedral vacancy sites. There are two distinct synthetic approaches available to produce superconducting alkali-metal-intercalated M_3C_{60} salts, namely, vapor transport and solution syntheses. The conventional thermal vapor transport synthetic procedure involves only the mixing and heating of stoichiometric amounts of alkali metal or M_6C_{60} and C_{60} in a sealed tube[3−5] and is considered to be a reliable method of producing phase-pure superconducting fullerides. However it is very time-consuming due to the nature of the heterogeneous solid-state reaction. Douthwaite et al.[6] recently reported a rapid synthesis of alkali-metal fullerides using a microwave-induced argon plasma (MIAP), in which the MIAP accelerates both mass transport of alkali-metal vapor to the C_{60} surface and diffusion of the alkali-metal cation into the C_{60} lattice, thereby substantially reducing the reaction time to the order of seconds.[6] The drawback of the MIAP route is that it is difficult to control the stoichiometry of products during the first stage of microwave synthesis. “Solution” routes to M_3C_{60} (M = K, Rb) using toluene,[7] tetrahydrofuran (THF),[8] or ammonia[9,10] have also been reported. The term “solution” is used loosely, since there is only partial solubilization of the ingredients in some of these methods. The sample prepared from toluene or THF has residual solvent effects and the need for using excess alkali metal, which causes great difficulties in achieving the desired stoichiometry of the final product. In addition, M_3C_{60} samples (M = K, Rb) prepared from these solvents often show a quite small superconducting shielding fraction. The liquid ammonia synthetic route produces superconducting M_3C_{60} phases with reasonable shielding fractions; however, one of the limitations of this method is that the reaction has to be conducted in the liquid ammonia temperature region of −78 to −33 °C. In addition, a recent study from this laboratory[11] shows that samples synthesized from liquid ammonia contain residual NH_3 molecules which prohibit the direct formation of a fcc superconducting M_3C_{60} phase. As a consequence, dynamic pumping for a few days followed by further annealing at higher temperature is required in order to remove residual NH_3.

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1997.

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S0897-4756(97)00392-X CCC: $14.00

Pure C_{60} and C_{60}^{n-} anions exhibit remarkable differences in terms of their solubility properties. The "solution" synthesis of alkali-metal fullerides clearly shows that C_{60}^{n-} anions are very soluble in liquid ammonia, forming a reddish brown solution, as compared with the very limited solubility of pure C_{60} in the solvent. Alkylamines share some of the solvent properties of liquid ammonia. For example, C_{60}^{n-} anions are readily soluble in methylamine, propylamine, and other alkylamines. However they undergo addition of several amine molecules across the 6/6-MR double bonds of the fullerene cage. Earlier work from this laboratory has described the preparation of M_3C_{60} salts from methylamine solution,[12] which extends the operating temperature range up to the boiling point of liquid methylamine (−6 °C). In this work, a direct reaction between a stoichiometric mixture of Rb and C_{60} (with molar ratio Rb:C_{60} = 3:1) at room temperature utilizing propylamine and butylamine as solvents is reported.

Experimental Section

The C_{60} was purchased from Hoechst with purity >99% (Gold Grade) and was subjected to dynamic pumping at 200 °C for 2 h prior to use. Rubidium metal (99.8%) was obtained from Aesar and was used without further purification. The *n*-propylamine (>99%) and *n*-butylamine (>99%) were obtained from Aldrich Chemicals and were dried and freshly distilled over KOH under an inert atmosphere before using. All material transfers were conducted inside a glovebox which had oxygen levels less than 2 ppm and moisture less than 3 ppm. Stoichiometric amounts of C_{60} (100 mg) and Rb metal were placed into a round-bottom flask that contained about 25 mL of a solvent (propylamine or butylamine). The system was purged constantly with argon to avoid oxygen and moisture interference.

The reaction was conducted at room temperature with constant magnetic stirring. During the first 60 min of reaction, the light green solution that was initially formed turned yellow and then brown as C_{60} reacts more and more with the solvent. C_{60} reacts with the large excess of amine under these circumstances to form $C_{60}(NH_2R)_x$, where x varies from 1 to 12.[13−15] Rb metal was found to remain as a solid during the first few hours of reaction but finally slowly dissolved. After 20 h of reaction, a homogeneous solution phase was formed with a dark reddish brown color.

After the reaction was complete, the reactor was connected to a vacuum manifold, and the solvent was evaporated at room temperature. The black powdery product was removed inside a glovebox, and no unreacted Rb metal could be observed. The product was heated at 125 °C under dynamic vacuum for 2 days, followed by further annealing at 375 °C for an additional 2 days in a sealed glass tube. Thermal analysis was performed using a differential scanning calorimeter (DSC 2920, TA Instruments). X-ray diffraction (XRD) spectra were taken on an INEL powder diffractometer (Cu Kα, 1.5406 Å). The magnetic susceptibility was measured using a Quantum Design SQUID magnetometer.

Results and Discussion

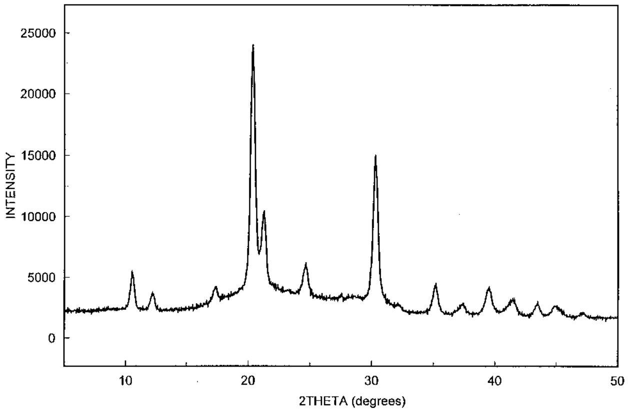

Figure 1. XRD powder pattern of the Rb_3C_{60} sample.

Figure 1 shows the room-temperature XRD pattern of Rb_3C_{60} obtained from butylamine solution after thermal treatment. All diffraction peaks appearing in the spectrum can be indexed on the basis of a fcc unit cell with a lattice constant of 14.43 ± 0.02 Å, slightly larger than the value of 14.39 Å for Rb_3C_{60} obtained from a vapor transport preparation[4] but in good agreement with the value reported from a liquid ammonia synthesis[16] (14.45 Å) or from a liquid methylamine preparation[12] (14.43 Å). This XRD diffraction pattern, combined with the calculated lattice constant, is characteristic of a pure fcc Rb_3C_{60} phase. DSC analysis has been performed on samples both before and after thermal treatment. For the "as-made" sample (the sample without thermal treatment), DSC experiments did not detect any phase transition in the temperature region −25 to −10 °C, indicating that little or no unreacted C_{60} is present. There were no structural phase transitions observed for the sample after thermal treatment with temperature up to 400 °C, indicating that the Rb_3C_{60} phase thus produced is thermally stable. A solution ^{1}H NMR experiment (with dimethyl-d_6 sulfoxide as the solvent) shows only resonance associated with traces of water in the solvent, and there was no evidence of existing residual hydrogen in the Rb_3C_{60} sample obtained from propylamine or butylamine after thermal treatment.

Figure 2 shows the temperature dependence of the magnetization for two samples that were heated at 125 °C under dynamic vacuum for 2 days, followed by additional annealing at 375 °C for another 2 days (for sample a) and for another 7 days (for sample b). The onset superconducting transition temperature (T_c) is 28 K as shown in the inset of Figure 2. A very slow decrease in magnetization is found in the region just below T_c, which becomes much more rapid when the temperature is lower than 26 K. This type of transition has been interpreted in terms of weak links between fine superconducting grains.[17] The shielding fraction at a temperature of 5 K is calculated to be ~5% in comparison with a perfect superconductor of cylindrical geometry. The T_c values found in the present samples are lower than the onset temperature of 29.5 K found in a Rb_3C_{60} sample prepared by the vapor transport method and are very close to that of Rb_3C_{60} prepared from an NH_3 solution.[11] Although the mechanism causing the depression of the superconducting transition

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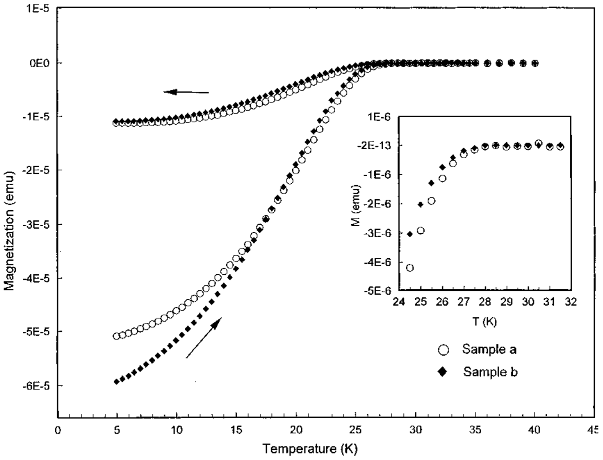

Figure 2. Temperature dependence of the magnetization of Rb_3C_{60}. Samples a (open circle) and b (solid diamond) were heated at 125 °C under dynamic vacuum for 2 days, followed by additional annealing at 375 °C for another 2 days and for another 7 days, respectively. The applied magnetic field was 20 G. Upper curves, field cooled; lower curves, zero field cooled.

temperature is not fully understood at present, it has been speculated that it might be related to the orientational disorder of C_{60} ions within the crystal unit cell resulting from thermal elimination of solvent from the Rb_3C_{60} crystal lattice.

Rb_3C_{60} samples produced from various amine solvents are almost identical in terms of their fcc unit-cell lattice constants,[12,16] indicating that there is a minimal effect due to residual solvent. Previous studies have shown that superconducting fullerides M_3C_{60} (M = K, Rb, and various alkali atoms) can reversibly absorb or release ammonia molecules. As a consequence, the formed ammoniated fullerides $(NH_3)_xM_3C_{60}$ exhibit either remarkable lattice expansion of the fcc unit cell,[18] or the original fcc unit cell is greatly distorted or even disrupted.[19,20] Those well-defined XRD peaks from the fcc Rb_3C_{60} lattice shown in Figure 1, as well as a ^{1}H NMR experiment reveal that the thermal treatment employed in this work will sufficiently remove solvent molecules from the reaction product synthesized from alkylamines. This implies that not only are any intercalated amine molecules removed but also all amine adducts are decomposed quantitatively.

Although ammonia and alkylamines share some of the same properties and intercalated fullerides Rb_3C_{60} produced from various amine solvents appear to be identical after thermal treatment, the intercalation reaction mechanisms appear to be very different. In the liquid ammonia synthetic route, the alkali-metal intercalation reaction can be considered to be a stepwise process. The initial reaction involves the formation of an electron-solvated solution. This electron-solvated solution has a characteristic intense blue color, which can be observed at the moment liquid ammonia is condensed into the reactor.[9,12] The second step is the charge-transfer between C_{60} powder and solvated electrons. This process produces $C_{60}{}^{n-}$ anions, which are readily soluble in liquid ammonia to form a dark reddish brown solution.[9,12,16] On the other hand, the alkali-metal intercalation in alkylamine solvents at room temperature might occur by a completely different reaction mechanism, suggested by color changes typical of a reaction between C_{60} and primary amines forming amino−fullerene adducts.[13] Apparently charge transfer occurs between Rb metal and the newly formed amino−fullerene adduct, as indicated by the dissolution of Rb metal and the appearance of a dark reddish solution. Although nucleophilic attack between C_{60} and liquid ammonia cannot be excluded theoretically, this reaction must be very slow at the low operating temperature employed in the liquid ammonia method (from −78 to −33 °C). In fact, pure C_{60} can be recovered unchanged after being kept in liquid ammonia for 2 h, a typical time scale for an alkali-metal intercalation reaction in liquid ammonia.

It has been proposed that the high electron affinity of a C_{60} molecule originates from six interconnected pyracyclene moieties, on the basis of the premise that pyracyclene is a $4n\pi$ system.[13] The reaction between C_{60} and amines is, therefore, a typical neutral nucleophilic addition reaction. It involves the formation of a $C_{60}{}^-$ anion as an intermediate species followed by the formation of C−N and C−H covalent bonds. This study indicates that a direct reaction between C_{60} and butylamine at room temperature produces amino−fullerene adducts with an average of about six amine molecules added to each C_{60}, as characterized by elemental and thermogravimetric analysis weight loss measurements. On the basis of the experimental observations, the proposed charge-transfer between Rb metal and the C_{60}−amine adducts in propylamine or butylamine takes place in a similar way to the charge transfer found between Rb and C_{60} in a liquid ammonia system, indicating that the reactivity of C_{60}−amine adducts is comparable to the reactivity of pure C_{60}. It is important to realize that the amine addition reaction actually functionalizes fullerene C_{60} and changes its solubility property. The name fulleroid[21] is used for such a functionalized fullerene that possesses electronic properties similar to those of a pure fullerene while possessing modified physical and/or chemical properties, depending on the functional group attached.

Conclusions

Rubidium metal intercalated fullerene Rb_3C_{60} can be synthesized by a direct reaction between a stoichiometric mixture of Rb and C_{60} using propylamine or butylamine as solvents, followed by vacuum thermal treatment. The reaction setup is greatly simplified over the liquid ammonia method since the reaction can be conducted at room temperature. However, it takes a longer time to complete the reaction due to the slow reaction rate, and the sample must be subsequently annealed to higher temperatures. A stepwise mechanism is proposed as the reaction produces amino−fullerene adducts first, followed by charge-transfer between the adduct and Rb metal. The reactivity of amino−fullerene adducts appears comparable to that of pure fullerene C_{60}.

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