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Synthesis of Fullerides of Alkali and Alkali-Earth Metals Under Mechanical and Chemical Activation

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The synthesis of fullerides of alkali metals (Na, K) and alkali-earth metals (Sr, Ba) was performed under the mechanical and chemical activation in the organic solvent. Under mechanical activation of synthesis the time of the complete transformation depends on: i) the nature of solvent, ii) ratio metal/fullerenes and iii) the chemical activity of metal and method of synthesis.

Keywords: fullerides, nuclear magnetic resonance, mechanical activation

INTRODUCTION

The most popular synthesis method of fulleride with alkali metals M_nC_{60} now is a gaseous method [1]. However this method is not effective for synthesis of fullerides with $n<3$ which transform under high temperature to the more stable compounds with $n\geq3$. Low temperature methods of synthesis of these substances in organic and non organic solvents seems to be more promising [2]. In this paper we report on investigation of reactions of synthesis of fullerides with of Na, K, Sr and Ba in different organic solvents under mechanical activation which makes a reaction fast, complete and under soft condition [3].

EXPERIMENTAL

High energy milling of the powder of Na/C_{60} {the ratio of components was (1÷6):1} and $Ba(Sr)/C_{60}$ {the ratio of components was (6÷10):1} was produced in hermetic ZrO_2 ball-mill. As an organic solvent we used distillated with $LiAlH_4$ tetrahydrofuran (THF), toluene, pentane, hexene, dodecene, which are inert solvents with donor properties. The mixture then was placed into Shlenk vessel and solvent was removed by heating at T<40°C under vacuum. Low energy milling of mixture M/C_{60} (M=Na, K) with ratio of component 3:1 was performed in glass ampoule in the presence of glass ball. The same ampoule was used for NMR measurements.

Black and brown powders synthesized by the first method and suspension in ampoule were investigated by ^{13}C and ^{23}Na NMR with help of AC-200 (Bruker) in magnetic field B=7.04 T at frequency 50.323 MHz (^{13}C) and 52.92 MHz (^{23}Na). Pulse duration was 4 μs, repetition time was 4 s, number of scans was 4000 at T=300K. Superconducting properties of K_3C_{60} were investigated by standard radiofrequency method at low frequency in the same ampoule as was for NMR.

RESULTS and DISCUSSION

According to our results high boiling temperature solvent with high solubility of C_{60} allows to increase the temperature of synthesis of fullerides as compared with low boiling temperature solvent with low solubility of fullerenes (pentane for example). The percentage of fullerides with alkali and alkali-earth metals in a high energy milling reactor is higher under higher temperature of synthesis.

Nevertheless in the presence of alkanes the formation of fullerides with Sr and Ba was not performed even during 10 hours in dodecane which gives the possibility to increase the temperature of reaction to 80-90°C (in pentane the temperature of reaction is only 40°C) and ratio of components to ≥6:1. We

suppose the low rate of reaction is connected with the low solubility of fullerene in these solvents, sometimes there is no solubility of fullerides at all. The rate of reaction increases in THF which is a weak solvent for fullerides. The maximal rate of interaction of components was in toluene.

The ^{13}C NMR data in toluene show three peaks (Fig. 1a). The fist one at 145 ppm corresponds to pristine retaining fullerene (145 ppm). The others assimetrical peaks in the region 180÷220 ppm correspond to fulleride ions. Nevertheless according to ^{13}C NMR (Fig. 1a) even in this case intercalation of C_{60} by Sr or Ba during 10 hours with 10 Moles of metal to 1 Mole of C_{60} does not lead to the formation of single-phase sample and the reaction of all fullerene.

The best results were obtained in a reaction of fullerene with Na which is more active then Ba or Sr. The little excess of Na during synthesis of Na_3C_{60} leads to the formation of Na_3C_{60} during 3 hours. The absence of C_{60} after the reaction may be easy controlled by ^{13}C NMR and vanishing of colour of toluene solvent. In this case the sample for NMR was fabricated by drying under vacuum. The typical NMR spectrum for such samples shown in Fig. 1b. There is only one wide peak at 178 ppm, corresponding to perfect Na_3C_{60} synthesized in direct reaction between C60 and the alkali metal vapor. If the ratio was $Na:C_{60}=1\div3:1$ then the wide peak was observed at 170-220 ppm (Fig. 1c). This peak corresponds to different states of fullerene. The narrow 144 ppm peak deals with initial fullerene. Kinetics of intercalation of metal in fullerene may be easy investigated in glass ampoule for NMR under low energy milling during the synthesis of fullerides M_3C_{60}. In Fig. 2a the ^{13}C NMR spectrum is shown for mixture of $3Na+C_{60}$ which was measured immediately after obtaining of the colourless solution of toluene. This spectrum contains only one wide peak at 180-240 ppm that is different from asymetrical peak of low

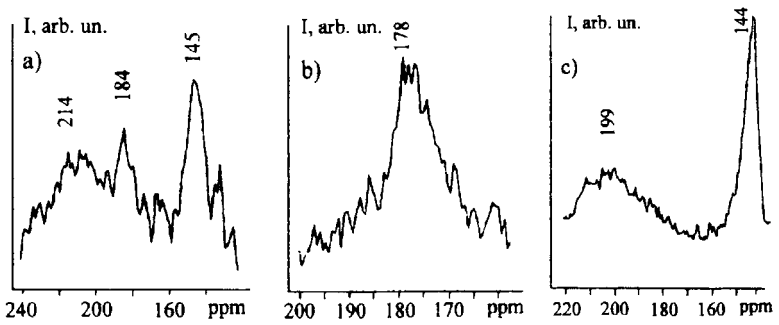

FIGURE 1 The ^{13}C NMR spectrum of (a) C_{60} intercalated by Sr or Ba during 10 hours; (b) of Na_3C_{60}; (c) for the sample synthesized from mixture of Na and C_{60} in ratio Na:C_{60}=1÷3:1.

temperature state of C_{60} at 33-213 ppm [4] and may be attributed to superposition of ^{13}C NMR peaks of fullerides of different composition. Our ^{23}Na NMR data also shows three peaks at 294 ppm, 220 ppm and 1133 ppm. The last peak is due presence of metal, the first two peaks are due to cations of Na in fullerides. Interesting discussion of NMR data may be found in ref. [5]. Thus, the presence of metal means that the loss of colour of solution does not mean the formation of Na_3C_{60}.

Indeed, annealing of a sample at 100 °C during 20 days leads to appearance in the ^{13}C NMR signal of one broaden peak at 190 ppm which is shown in Fig. 2b. In ^{23}Na spectrum the signal of the free metal disappears, intensity of 220 ppm peak decreases relatively to 290 ppm peak.

The same reaction under the same condition for mixture of $3K+C_{60}$ leads to one broaden peak in ^{13}C NMR spectrum at 197 ppm which is shown in Fig. 3a. 20 days annealing at T=100 °C leads to more narrow peak and shears it to strong field (189 ppm, Fig. 3b). The sample according to NMR data was single-phase, nevertheless the superconducting transition in K_3C_{60} synthesized under low energy grinding was observed at T≈15K for ≈50% of the volume of

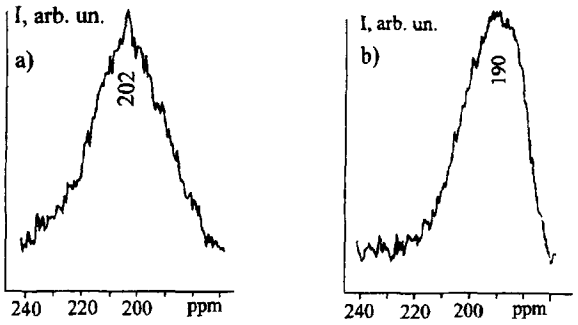

FIGURE 2 The ^{13}C NMR spectrum for (a) sample synthesized from mixture of $3Na+C_{60}$ at the initial stage of synthesis; (b) for the same sample annealed at T=100 °C during 20 days

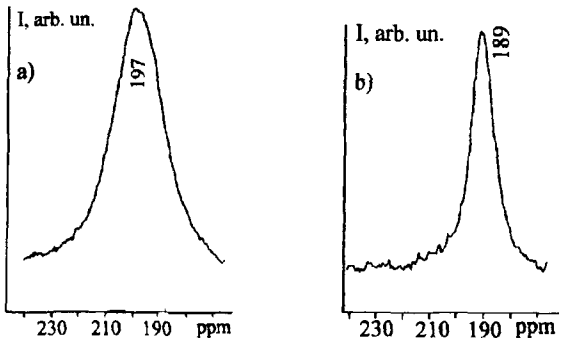

FIGURE 3 The ^{13}C NMR spectrum (a) for sample synthesized from mixture of $3K+C_{60}$; (b) for the same sample annealed at T=100 °C during 20 days

the sample. The measurements were performed in the sealed ampoule in the presence of solvent. We suggest that solvent was partly intercalated in C_{60} and this suppressed the superconductivity. The superconductivity may be suppressed also due to amorphous state of sample.

Very interesting kinetics of metal intercalation was observed for liquid at room temperature alloy $Na_{0.7}K_{2.3}$. 20 hours heating at 70°C leads to appearance in the ^{13}C NMR spectrum broaden peak at 200-210 ppm with and a peak of pristine C_{60} at 146 ppm with the same area. In the ^{23}Na NMR spectrum we

observed a peak at 1472 ppm from the NaK alloy (area of Na - 50%), two peaks at 347 ppm and 274 ppm from fullerides (which corresponds to -45% of the total Na content) and weak peak from Na at 1135 ppm (-5%). Annealing the sample leads to the shift of two peaks of Na in fullerides in higher fields and simultaneously decreasing of the Na content in fulleride down to 25%. Intensity of the signal from alloy increases up to 75% and corresponding peak shifted to 1415 ppm. Thus under intercalation of C_{60} by Na/K alloy Na at first reacts with fullerene and then Na is replaced by more active K.

CONCLUSION

Under the mechanical activation of synthesis the time t_0 of the complete transformation depends on three main factors: i) the first factor is the nature of solvent. Time t_0 increases in the sequence of solvent from toluene - THF to dodecene, hexene, pentane. This time t_0 depends on the solubility of fullerenes in organic solvent. ii) Time t_0 depends also on ratio metal/fullerenes and has a minimal value at $M/C_{60}>6$. iii) The third factor is the chemical activity of metal and method of synthesis.

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NOTE OF THE REFEREE : 1) The too wide 144 ppm free C_{60} line of Fig. 1c is probably saturated due to a too short repetition time (4 s).
2) Main broad lines in the range 180-200 ppm could be the Ho//a,b components of the more extended static chemical shift tensor as in Fig 1a and 1c. Not enough basis line is shown to realize if the apparent symmetry should not be due to an approximate phase adjustment in the presented too small frequency window.