

STABILITY OF C₆₀ FULLERENE UNDER THERMAL TREATMENT IN HYDROCARBONACEOUS SOLVENTS

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Abstract

The stability of fullerenes in low concentrations in boiling toluene under reflux was studied in order to answer some of the questions raised in previous works dealing with extraction and analysis of fullerenes from rocks. It was observed that small concentrations of C₆₀ fullerene in the toluene (10 mg l⁻¹) were highly susceptible to any trace of molecular oxygen (or any other oxidizing agent) and quickly decomposed. This was accompanied by change of color of the solution from light violet to pale yellow, typical for oxidation adducts of fullerenes. Various grades of toluene purity and C₆₀ standard were tested, as well as toluene deoxygenation before the treatment and keeping the apparatus under argon. However, only bubbling of argon through the boiling solution during the whole experiment was able to quench the decomposition of C₆₀. This finding has serious consequences on results of extractions made by higher temperature treatments (e.g. Soxhlet), reported earlier by other groups. The decomposition in experiments with no safety precautions against oxygen takes place also in solutions with higher concentrations of C₆₀ (1 g l⁻¹), the loss being “only” ca. 5%. This shows that only a limited number of reactive species is readily available to decompose C₆₀. ¹³C nuclear magnetic resonance showed that the principle products of pure toluene oxidation are benzoic acid, benzylalcohol and benzaldehyde. Comparative experiments were performed in cyclohexane and n-heptane (initial concentration of 10 mg l⁻¹), only negligible loss of fullerenes was observed.

Introduction

Up till now, naturally occurring fullerenes have been reported in rocks that experienced unique geological events under highly energized conditions, such as lightning, meteoritic impacts (Sudbury, Gardnos, Ries), or impact related event at the Cretaceous–Tertiary (K-T) and the Permian–Triassic (P-T) boundaries. In addition, fullerenes or similar structures have been described in Allende and Murchison carbonaceous meteorites, in the Tagish Lake meteorite and in a microcrater on the Long Duration Exposure Facility (LDEF) satellite. More detailed reviews are given by Buseck (2002), Heymann et al. (2003) and Frank (2005). A different group of rocks containing natural fullerenes includes shungites from Karelia, Russia (e.g. Buseck et al., 1992), and hard solid bitumens (HSB) from Mítov, Czech Republic (Jehlička et al., 2003). It has to be mentioned that the highest reported concentration of fullerenes so far was 12 mg l⁻¹.

The occurrence of natural fullerenes still raises many questions considering their formation and long-term stability in a host rock. Most of these issues closely resemble problems encountered in laboratory procedures. One of them is the stability of fullerenes in organic solvents under higher temperatures, which is very important for fullerenes found in solidified bitumens like in Shunga or Mítov localities. Such knowledge is also essential to ensure the highest possible yield during fullerene extraction performed by for example Soxhlet extraction. This can be applied not only to a successful extraction of trace concentration of fullerenes from rocks, but also from fullerene soots. However, in such case the concentration level is at least around three orders of a magnitude higher than in a rock!

We therefore tested the rate of decomposition of C₆₀ fullerene in boiling toluene and other hydrocarbonaceous solvents under various conditions. The loss of fullerenes was quantified using high-performance liquid chromatography (HPLC). Principles of the decomposition are discussed and proper treatment is suggested to reduce the loss of fullerenes during the extraction.

Methods

In general, following procedures were used. Stock solutions of C₆₀ standard (SES Research, 99.5+ % purity) in toluene (Merck LiChrosolv, HPLC grade) in concentration 10 mg l⁻¹ were freshly prepared before each individual experimental batch. In some experiments, toluene (Supelco, HPLC grade), cyclohexane (Scharlau, HPLC grade) and n-heptane (Aldrich Chromasolv, HPLC grade) were used as alternative solvents. In one experiment, different C₆₀ standard (Hoechst Gold Pick) has been used. The experimental conditions for different samples are summarized in Table 1. In each experimental batch,

three replications were performed simultaneously as follows: 50 ml of the stock solution was boiled under reflux for 8 hours in darkness, let cool to room temperature, added pure solvent to 50 ml when needed and analyzed by high performance liquid chromatography (HPLC). In the case of cyclohexane and n-heptane, the remaining solutions after boiling were evaporated to dryness on a rotary evaporator and redissolved in 50 ml of toluene. For HPLC analyses, 200 mL of extract were injected in the semipreparative Cosmosil Buckyprep column (250 mm x 10 mm) equipped with guard column Buckyprep type Watrex (20 mm x 10 mm). Toluene was used as a mobile phase at a flow rate of 3 ml/min. At least two measurements were carried out for each extract and results are represented here as mean values from these measurements. A photodiode array (PDA) detector (Well Chrom, Knauer) was employed to detect photometrically fullerene in the eluent at 330 nm.

Results and discussion

The experimental conditions and average C_{60} yields are summarized in Table 1. As can be seen, C_{60} decomposes readily (yield < 7%) when boiling in toluene under air, regardless the particular toluene. The yield was better (ca. 15%) when the solution was bubbled with argon prior to the boiling and the whole apparatus was kept under Ar during the experiment (but not bubbled). Far better result was achieved when the solution was bubbled with Ar during the whole experiment (# IX, C_{60} yield ca. 93%). However, the yield was not complete too. The best results were achieved when C_{60} was boiled in cyclohexane or heptane (>99%). An interesting result is presented in # X where C_{60} was boiled in toluene in air but its starting concentration was 1 g l^{-1} , i.e. 0.1 %. In this case the C_{60} yield was ca. 94%, however, the molar loss was much higher than in case with 10 mg l^{-1} C_{60} starting concentration.

Table 1. Experimental conditions and average C_{60} yields after 8 hours of boiling. *:TM - toluene Merck, TM2 - toluene Merck different batch, TS - toluene Supelco, Hep - n-heptane, CH - cyclohexane; **:SES – C_{60} standard from SES Research, H - Hoechst

#	Solvent *	C_{60} **	C_{60} conc. (mg l^{-1})	Conditions	C_{60} yield (%)	C_{60} loss (μmol)
II	TM	SES	10	air	3.4	0.671
III	TM2	SES	10	air	6.9	0.647
IV	TM	H	10	bubbled with Ar before experiment, sealed under Ar during experiment	14.9	0.591
V	TS	SES	10	air	<1	>0.688
VI	Hep	SES	10	air	99.7	0.002
VIII	CH	SES	10	air	99.6	0.003
IX	TM	SES	10	bubbled with Ar during experiment	92.8	0.050
X	TM	SES	1000	air	93.7	4.391

Four selected chromatograms are presented in Figure 1, comparing the untreated C_{60} standard in 10 mg l^{-1} concentrated toluene solution (red line) to C_{60} boiled in toluene in air (green line), C_{60} boiled in toluene with bubbling Ar (black line) and C_{60} boiled in cyclohexane in air (blue line). The principal feature of all chromatograms except C_{60} boiled in toluene in air is the peak with elution time ca. 12.8 min corresponding to C_{60} . Beside this, a couple of additional minor peaks occur at earlier retention times, especially an unresolved mixture at around 5.5 min for the C_{60} boiled in toluene in air. These are ascribed mainly to benzaldehyde and benzylalcohol, and also partially to benzoic acid based on the comparison with standards and ^{13}C NMR measurements. All these substances are toluene oxidation products.

Also in other cases the area of these peaks inversely correlates to the area of C_{60} peak, i.e. the higher the concentration of toluene oxidation products, the lower the C_{60} yield. This may be partially prevented by careful preparation of the toluene and the experimental procedure using argon not only as a protective atmosphere but also to use argon to bubble through the boiling solution. However, this procedure is not ideal too, especially when used in a more complex set-up like the Soxhlet extractor. For low C_{60} concentration (lower than the solubility of C_{60} in the appropriate solvent), which can be expected in geological samples, an alternative solvent like n-heptane may be used.

As shows from the experiment with higher starting C_{60} concentration, only limited number of reactive species is available for the decomposition of (or addition to) C_{60} .

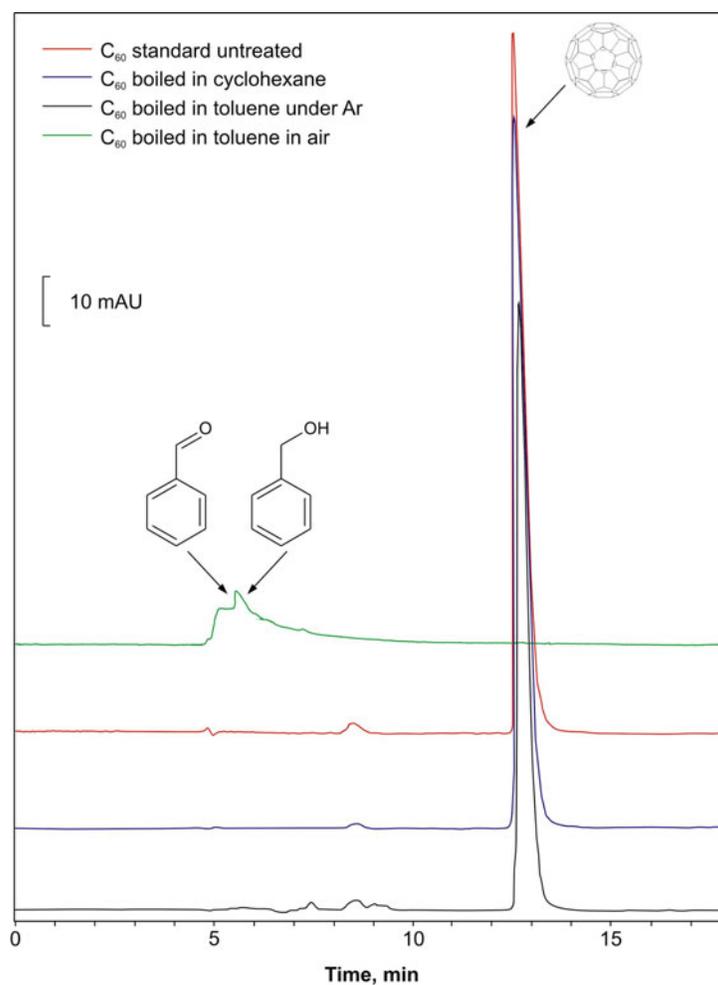


Figure 1. Chromatograms of untreated C₆₀ standard toluene solution (red line), C₆₀ boiled in toluene in air (green line), C₆₀ boiled in toluene with bubbling Ar (black line) and C₆₀ boiled in cyclohexane in air (blue line). The starting C₆₀ concentration was 10 mg l⁻¹ in all cases.

Conclusions

The almost complete C₆₀ fullerene disappearance in boiling toluene solutions is observed especially when the starting concentration was close to samples with geological origin, i.e. 10 mg l⁻¹. Thorough bubbling of the boiling solution with Ar prevents the loss only partially. For trace C₆₀ concentrations, an alternative solvent for high-temperature extraction could be used, like n-heptane.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic project Nr. 205-06-P348.

References

- Buseck, P. R. 2002. Geological fullerenes: review and analysis. *Earth and Planetary Science Letters* 203(3-4): 781-792.
- Buseck, P. R., Tsipursky, S. J., Hettich, R. 1992. Fullerenes from the Geological Environment. *Science* 257(5067): 215-217.
- Frank, O. 2005. Origin of Fullerenes in Rocks. PhD Thesis. Charles University in Prague, Faculty of Science, Prague, Czech Republic.
- Heymann, D., Jenneskens, L. W., Jehlička, J., Koper, C. and Vlietstra, E. 2003. Terrestrial and extraterrestrial fullerenes. *Fullerenes Nanotubes and Carbon Nanostructures* 11(4): 333-370.
- Jehlicka, J., Svatos, A., Frank, O., Uhlík, F. 2003. Evidence for fullerenes in solid bitumen from pillow lavas of proterozoic age from Mitov (Bohemian Massif, Czech Republic). *Geochimica et Cosmochimica Acta* 67(8): 1495-1506.