



Mechanism and number of adducts of photo-addition of glycine methyl-ester to [60] fullerene



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ARTICLE INFO

Article history:

Received 4 April 2013

Received in revised form 1 June 2013

Accepted 6 June 2013

Available online 14 June 2013

Keywords:

Fullerenes

Photo-addition

Pyrrolidines

Azomethine ylide

HPLC–MS

Dimers

ABSTRACT

Recently, it has been shown that visible light irradiation of a mixture of C₆₀ and glycine methyl-ester in the presence of oxygen is a direct route to sequentially synthesize higher FP poly-adducts. However, the involved mechanism and the maximum number of pyrrolidine adducts per C₆₀ molecule remained to be ascertained. Using high resolution mass spectrometry and HPLC–MS, we show here that the most probable mechanism involves a first step of azomethine ylide (AMY) formation followed by its [2+3] cyclo-addition to C₆₀, and that the hexakis-adduct is the highest FP poly-adduct (FPPA) obtained under these conditions. Some FPPA and AMY dimers are also identified in the final mixture.

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1. Introduction

Recently, it has been shown that photo-additions to C₆₀ may be a facile route for C₆₀-polyadduct synthesis.¹ The authors showed that the irradiation of a mixture of glycine-methyl-ester (GME) and C₆₀, irrespective of the equivalent ratio (GME/C₆₀=0.5–200), does lead to the sequential formation of fulleropyrrolidine (FP) poly-adducts (FPPA) resulting from the addition of two GME radicals and the departure of a hydrogen peroxide and an ammonium molecule at each step. While the authors identified all reaction products including H₂O₂, NH₃, FP, and some FPPA, the mechanism of FP formation remained to be ascertained and the maximum number of pyrrolidine adducts per C₆₀ molecule has not been determined.

As the authors did not detect any GME-C₆₀ mono-adduct in the reaction mixture they proposed two possible mechanisms of FP formation.¹ The first one involves the concomitant addition of two GME radicals followed by an unprecedented cyclization mechanism involving NH₃ departure. The second one¹ involves several steps

leading to azomethine ylide,^{2–4} which undergoes a [2+3] cyclo-addition to C₆₀ leading to the FP derivative.

Among the different reaction intermediates of the two mechanisms proposed previously,¹ azomethine ylide (AMY) can be considered as the key point. The presence of the latter in the reaction mixture can be considered as the marker of the second mechanism, otherwise the first proposed mechanism must be considered. To check this assumption we used HRMS and HPLC–MS to systematically investigate the composition and the evolution of the reaction mixture during irradiation. In order to determine the mechanism and the number of adducts involved in the photo-addition of GME to C₆₀ we investigated the kinetics of FP formation during irradiation of C₆₀ in the presence of a large excess of GME (1/200, equiv/equiv).

2. Results and discussion

2.1. HRMS

Fig. 1 shows the ESI-HRMS spectra observed after direct infusion of the reaction mixture (C₆₀/GME, 1/200, equiv/equiv) obtained after 180 or 360 min of irradiation. As expected for polar compounds, such as those present in the mixture including FPPA and

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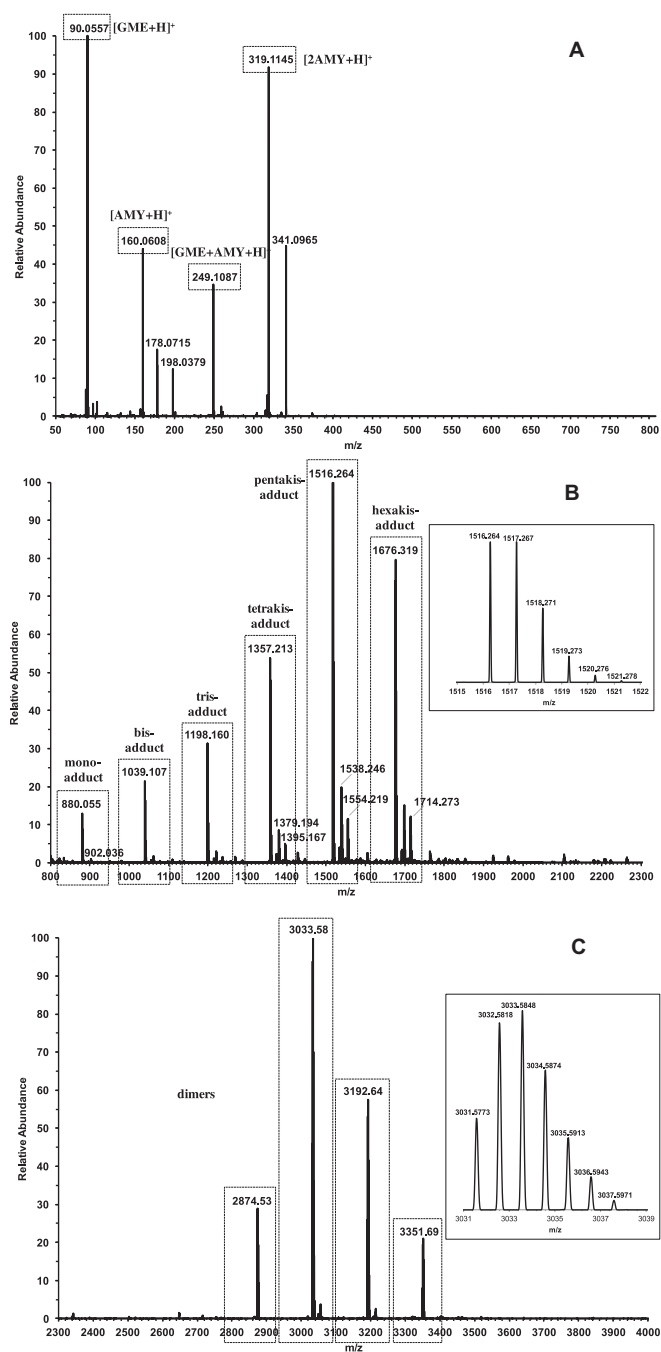


Fig. 1. High resolution mass spectra of the products present in the mixture after (A) 180 min and (B and C) 360 min of irradiation.

GME the ESI mode was more sensitive than the APCI mode. As the samples contain a wide variety of compounds with a wide range of m/z values, we performed three spectra with different mass ranges for each sample in order to obtain sufficient resolution. The first one encompasses the mass values ranging from 50 to 800 amu corresponding to the reaction intermediates after 180 min of irradiation (Fig. 1A). The second one is a spectrum in mass values ranging from 800 to 2300 amu mostly corresponding to FPPA (Fig. 1B). The third one is dedicated to mass values ranging from 2300 to 4000 amu, corresponding to other possible higher adducts (Fig. 1C). The second and the third spectra were performed after 360 min of irradiation in order to reach the end of the reaction corresponding to the saturation of C₆₀ molecules by the pyrrolidine adducts.

Table 1 summarizes the m/z values of all detected ions and their corresponding interpretation. The first spectrum (Fig. 1A) shows a peak at $m/z=90.0557$ amu corresponding to the m/z ratio of [GME+H]⁺, and a peak at $m/z=160.0608$ amu, corresponding to the m/z ratio of [AMY+H]⁺ accompanied by several other ions at $m/z=178.0715$ amu, 249.1087 amu, and 319.1145 amu attributed to [AMY+H₂O+H]⁺, [AMY-GME+H]⁺, and [AMY-AMY+H]⁺ species, respectively. The presence of AMY and notably AMY-GME and AMY-AMY (Fig. 1A) ions in the mixture favors the mechanism proposed previously involving AMY formation followed by its [2+3] cyclo-addition to C₆₀ leading to the FP formation.¹

The second spectrum (Fig. 1B) shows several groups of peaks corresponding to [FPPA+H]⁺, [FPPA+Na]⁺, and [FPPA+K]⁺ ions, because: 1—the difference of m/z between these groups of peaks is equal to 159.053 ± 0.002 amu. This value corresponds to the theoretical mass (159.0531 amu) of the pyrrolidine moiety; 2—the m/z values of the main peaks correspond to the expected masses of FPPA with calculated mass errors less than 10 ppm in all instances (Table 1); and 3—the isotopic distribution of the peaks in each group are fully consistent with the isotopic distribution expected for FPPA (Fig. 1B, inset).

These results show that the maximum number of observed pyrrolidine adducts on C₆₀ is equal to 6, which corresponds to the addition of 12 GME. It is worth noting that the maximal number of adducts exactly corresponds to the number of pyracylene units. This relatively limited number of adducts is likely to be assigned to steric hindrance and/or to the alteration of the core geometry of the fullerene creating distortion in the vicinity of the site of adduct formation. Indeed, it is well known that the additions are exothermic and are presumably driven by the relief of strain in the C₆₀ cage resulting from the pyramidization of its sp² to sp³ carbon atoms.^{5–8} The exothermicity of additions depends on the size and number of adducts grafted to the C₆₀ cage and decreases at a certain stage. As a consequence, adducts with a high degree of addition eventually become unstable, which limits the number of adducts. However in the present case steric hindrance must play a part because of the shapes and volumes of the cumbersome addends.^{5–8} A theoretical simulation will be necessary to distinguish the real driving force leading to this number of adducts.

The third spectrum (Fig. 1C) shows the presence of some unexpected peaks corresponding to FPPA dimers where FPPA are linked through two AMY molecules (Table 1, Scheme 1), as evidenced by the m/z ratio of 3351.69, 3192.64, 3033.58, and 2874.53 amu as well as by the expected isotopic distribution (Fig. 1C, inset). The highest m/z value corresponds to a hexakis-hexakis dimer (Scheme 1) while the other m/z values correspond to a hexakis-pentakis dimer, a pentakis-pentakis dimer, and a pentakis-tetrakis dimer, respectively (Table 1).

2.2. Kinetics of pyrrolidine addition

Fig. 2 shows the kinetics of pyrrolidine addition on C₆₀. As expected, the irradiation of the mixture with a large excess of GME leads to a rapid FPPA formation.¹ Two minutes after irradiation, the tris- and the tetrakis-adducts are detected but the mono- and bis-adducts are the main adducts present in the mixture.

Ten minutes after irradiation the concentrations of the mono and the bis-adducts decrease while the tetrakis-adduct becomes the main derivative. At this stage, pentakis- and hexakis-adducts are also detected. The tris-adduct also increases but less than the tetrakis-adduct does thus confirming the sequential addition of GME to C₆₀.¹ After 30 min of irradiation, the concentrations of the tris and tetrakis-adducts decrease with the concomitant increase of the pentakis- and hexakis-adducts. One hour after irradiation, the two latter derivatives, notably the pentakis-adduct, become predominant.

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