Alkylation and phenylation of [60]- and [70]-fullerenes by the reaction with ketones in the ionization chamber of a mass spectrometer

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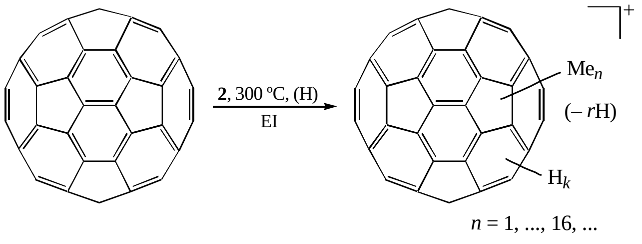
The title reactions proceed under electron impact (EI) and are accompanied by hydrogen addition and loss; the reaction of C_{60} with acetone has been shown to occur at least partly at the walls of the ionization chamber and experimental evidence suggests a radical path process involving EI generation of methyl radicals from acetone.

The reactions of fullerenes with other species in a mass spectrometer, though proceeding under special conditions (high energy of the ionising electrons, the absence of solvent *etc.*), provide valuable information on what can be successfully achieved in a flask and in what manner this can be done. The advantages of such a test for fullerene reactivity consist in that it requires only traces of reagents, the results can be obtained from relatively quick runs, and products are identified simultaneously. Recently we found that the reactions of C_{60} and C_{70} with the Scherer radical C_9F_{19} **1** in the EI ion source of a mass spectrometer resulted in trifluoromethylated fullerenes. The reaction substantially occurs at the walls of the ionization chamber by a radical mechanism involving the intermediate triflluoromethyl radicals formed from **1** by thermal dissociation and under EI. Accordingly, C_{60} attached up to 18 CF_3 addends when dissolved in 1,2,4-trichlorobenzene and reacted with **1** at 200 °C.[1]

Here, we report on the C_{60} and C_{70} reactions with ketones in the ionization chamber. We decided on ketones as reactants because of the fact that their molecular ions dissociate predominantly with the elimination of organic radicals to afford acyl cations. Thus, by analogy with the previous work,[1] radical reactions between fullerenes and ketones could also be anticipated to occur.

The experiments were performed on a 'Kratos MS890' mass spectrometer at an electron energy of 70 eV and an ionization chamber temperature of 300 °C (in some cases, 270 °C) by two procedures. Procedure A involved evaporation of a fullerene in the ionization chamber from a quartz needle, while a ketone was introduced *via* the GLC inlet. With procedure B, the ketone was evaporated from a capillary ampoule with the fullerene applied onto the outer surface of it (see ref. 1 for details).

The mass spectra obtained at the combined evaporation of C_{60} and acetone **2** by both of the procedures displayed the groups of ion peaks due to products of the methyl group addition to the fullerene core. These groups also contained ions formed by both hydrogen addition to the methylation products and hydrogen loss from them and/or their ions (Scheme 1 and Figure 1).



Scheme 1

The interaction of ketone **2** with C_{60}, C_{70} and endohedral metallofullerenes under conditions of the self-chemical ionization (self-CI) of **2** was studied.[2,3] The main products of these processes were identified as acetylfullerene cations. This difference can be attributed to the fact that the experiments were performed at a relatively high pressure in the ionization chamber (*ca.* 10 Pa) and at a rather low temperature (200 °C); at this temperature, fullerenes and their derivatives did not vaporise from the ionization chamber surface. Thus, only the products of gas-phase ion–molecule reactions were detected. By contrast, our experiments performed at a chamber temperature of 190 °C followed by an increase in the temperature up to 270 °C[†] and experiments performed at 300 °C with the 'filament switched off'[1] showed that the reaction occurred, at least partly, at the metal surface of the ionization chamber. A considerable amount of the products detected as ions (> 60%[‡]) vaporised from the walls of the ionization chamber, and EI was required for the process to proceed. The observed polyaddition, especially in the case of procedure B, agrees better with a surface process than with a gas-phase reaction. Furthermore, special runs were carried out with the ion-repelling electrode potential set to zero with respect to the ionization chamber, and the accelerating voltage (AV) turned off. If cation-involving reactions contribute significantly to the overall process, the amount of products can be expected to increase under these conditions.[§] Indeed, cations are forced out (extracted) from the ionization chamber to a lesser extent and more evenly distributed within the ionization chamber; thus, they attack the surface more evenly. However, only a small decrease (on the average, by about 20%) in the amount of the products evaporated from the ionization chamber surface and detected as the integral peak intensity of the first two ion groups (734–738 and 748–752 a.m.u.) was observed after switching AV on and returning the repeller potential to a standard value of +30 V. The decrease can be attributed to the alteration of the conditions under which a substance interacts with the electron beam. The aforesaid counts in favour of a radical path for the reaction involving the formation of intermediate methyl radicals from **2** under EI.[¶] The observed hydrogen addition and loss can be easily explained in terms of this mechanism.

The addition of methyl radicals to the fullerene core accompanied by hydrogen addition and loss was also found in the reaction between C_{60} and dibutyl ketone **3**. However, the monoisotopic (^{12}C) mass spectra derived from the aggregated magnet

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[†] C_{60} was applied to the inner surface of the ionization chamber at 270 °C using a quartz needle. Next, the temperature of the ionization chamber was reduced to 190 °C, and **2** was introduced *via* the GLC inlet. After 30 min, the temperature was again raised up to 270 °C. From the moment of the first appearance of the products until the main body of them had evaporated from the chamber surface, the peak intensities of the first two groups of ions (734–738 and 748–752 a.m.u.) were summarised over the magnet scans and then over the components of both of the groups. The integral intensity thus obtained was related to the similar value from the method A run performed subsequently on the same day at 270 °C.

[‡] This value may include a contribution from the products formed in the gas phase and condensed onto the surface of the chamber in the course of the reaction.

[§] The processes involving negative ions that could afford the detected products seem to be unlikely here.

[¶] Three possibilities may be taken into consideration for the formation of methyl radicals: (i) *via* dissociation of the molecular ion of **2**, (ii) *via* homolytic dissociation of acetone molecules in a superexcited state (the excited state with the energy higher than the first ionization potential),[4] (iii) the generation in the self-CI plasma of **2** because the pressure in the ionization chamber could be 10^{-2} Pa or higher when ketone **2** was introduced.

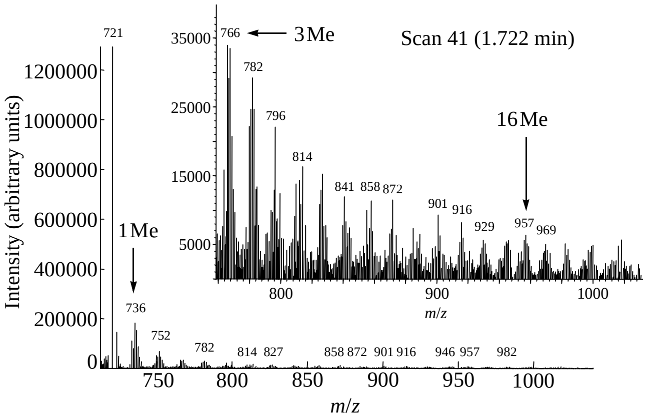

Figure 1 Mass spectrum recorded in the course of a run with C$_{60}$ and acetone **2** performed by procedure B.

scans and averaged over several runs performed by procedures A or B showed an ion peak at m/z 778 to be one of the most abundant peaks in the 776–784 a.m.u. group. This peak was considerably less abundant in the analogous spectra for the reaction between C$_{60}$ and **2**, whereas a peak at m/z 780 ($\mathrm{C_{60}Me_4^{+\cdot}}$) was among the dominant ones in the above group. This indicates that the butyl radical adds to C$_{60}$ in the reaction of the latter with ketone **3**. In addition, the mass spectra display ion peaks (of low intensities) at m/z 834 and 836, which can be ascribed to the $\mathrm{C_{60}Bu_2^{+\cdot}}$ and $\mathrm{C_{60}Bu_2H_2^{+\cdot}}$ ions (at least, these ions may contribute to the peak intensities). The aforesaid is in good agreement with the finding that, in the reaction of C$_{60}$ with phenylacetone **4**, the ions due to the addition of both methyl radicals and a benzyl group (toluene) were detected. The reaction between C$_{60}$ and acetophenone **5** gave rise to the ions of fullerene derivatives bearing up to four methyl groups and ions containing up to three phenyl groups. The ions of mixed derivatives (Figure 2) were also present in the spectra.

Analogously, C$_{70}$ reacts with ketones **2** and **5** adding methyl and phenyl radicals.

The EI–MS analysis of the reaction products obtained by UV irradiation of a mixture of C$_{60}$ with **5** during 13.5 h allowed us to detect fullerene derivatives containing from one to at least three methyl groups (some of the products had attached or lost hydrogen atoms) and that with a phenyl group (benzene) attached.[††] This agrees closely with the results obtained for the reaction with the same reactants in the ionization chamber.

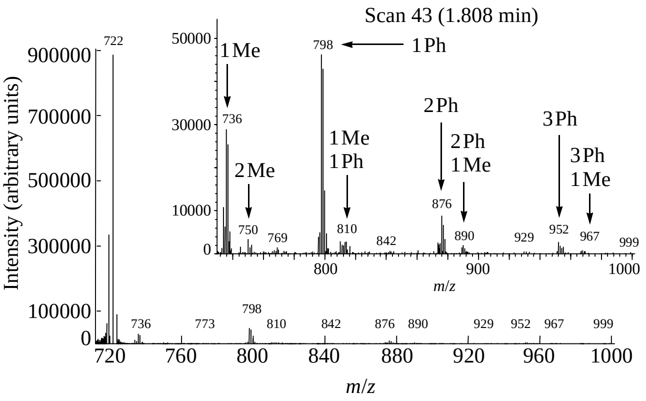

Figure 2 Mass spectrum from a run with C$_{60}$ and acetophenone **5** by procedure A (the ion peaks due to the products bearing three and four methyl groups are more pronounced in the spectra from other magnet scans). Higher intensities of the ion peaks due to phenyl derivatives than those of the corresponding methyl species can indicate that the former compounds are more stable (thermally and/or under EI).

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[††] Other products will be discussed in a subsequent publication.