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Laser-induced gas-phase synthesis of dimeric C_{70} oxides

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Abstract

The greater lability of C_{70} oxides towards oxygen release has been advanced recently to explain the failure to synthesise $C_{140}O$ from $C_{70}O$; by contrast the analogous reactions with C_{60} oxides result in the formation of fullerene oxide aggregates. The present report provides the first experimental evidence for the existence of oxides of the type $(C_{70})_2O_n$, resulting from gas-phase aggregation reactions when using matrix-assisted laser desorption/ionization to study synthetic, high performance liquid chromatography-purified C_{70} oxides. (Int J Mass Spectrom 184 (1999) L1–L4) © 1999 Elsevier Science B.V.

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Fullerene oxides have recently attracted much attention. A variety of synthetic methods [1–6] is at hand to introduce the epoxide functionality to fullerenes. Once the desired product is isolated, further possibilities for selectively modifying the fullerene surface are available. Fullerene oxides also show an interesting reaction behaviour both with themselves and in reactions with pure fullerenes. Upon heating either alone or in the presence of C_{60}, $C_{60}O$ readily produces the unusual, odd-numbered carbon cluster C_{119}, a reaction for which the liberation of CO [7–9] and CO_2 [10] has been verified. A rich variety of oxides of the type $(C_{60})_mO_n$ can be generated in reactions of $C_{60}O_n$ with C_{60}, from which $C_{120}O_n$ with $n = 1$, 2, and 3 [11–13] and $C_{180}O_2$ [14] have been structurally characterised. The bonding in these compounds features intact fullerene moieties connected by furanoid oxobridges. Most interesting in this context is the recent observation that pure C_{60} forms $C_{120}O$ simply on standing in air [15]. Kappes and co-workers managed to isolate and characterise three isomers of the mixed oxygenated dimer $(C_{60})O(C_{70})$, resulting from the reaction of $C_{60}O$ with C_{70} [16], and the vibrational spectroscopy of $(C_{60})_2O_n$, with $n = 1$ and 2 [16, 17] and $(C_{60})O(C_{70})$ [16] has been comprehensively investigated. Earlier attempts to synthesise $(C_{60})O(C_{70})$ and $(C_{70})_2O$ failed when using $C_{70}O$ as the oxygenated partner in the reaction with the respective fullerene [14]. On the basis of negative-ion laser desorption/ionization (LDI) experiments, a possible rationalisation of these findings was given in terms of a more facile loss of oxygen from $C_{70}O$ under the applied conditions [14]. Negative-ion LDI experiments conducted in the course of this investigation (spectra not shown) confirm this in that $C_{70}O$ shows a relatively more pronounced tendency to produce signals that

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correspond to the loss of oxygen than those due to the loss of CO or C_2, when compared to $C_{60}O$. A more conclusive insight can only result from a thermochemical description of the various species involved. However, at present, it seems reasonable to assume that a synthetic approach towards the hitherto undetected $(C_{70})_2O$ might require much milder reaction conditions than so far applied. The stability of all dimeric oxides discussed here has been confirmed by semi-empirical calculations [18].

Recently we have observed that gas-phase aggregation of C_{60} oxides can be achieved in matrix-assisted laser desorption/ionization (MALDI) experiments [19]. Based on the product distribution obtained from analytes of varying oxygen content and on varying the desorption/ionization conditions, it follows that the resulting $(C_{60})_mO_n$ aggregates possess the structural features of their synthetic counterparts derived from solution and solid state syntheses. In the present letter we report the successful application of this approach towards the formation of $(C_{70})_mO_n$ aggregates applying MALDI to C_{70} oxides embedded in a 9-nitroanthracene matrix and thus provide the first experimental evidence for the existence of these compounds.

The experiments have been performed utilising a commercial time-of-flight (ToF) mass spectrometer (Kompact MALDI IV, Kratos Analytical, Manchester, UK). This instrument has been applied in several recent investigations into the LDI behaviour of fullerene-based material covering the coalescence reactivity of highly fluorinated fullerenes [20], the formation of fullerenes from organometallic compounds [21], and the influence of delayed electron emission of fullerenes on the appearance of their postsource decay spectra [22]. For LDI, the instrument incorporates a nitrogen laser ($\lambda = 337$ nm) with a pulse duration of 3 ns. Although the linear flight tube of the instrument is followed by a reflectron (to which a curved field is applied), the mass resolving power achieved in the present experiments remained in the region of several hundred and was clearly insufficient to resolve the isotopic pattern of the C_{70} oxides. A reason for the low resolving power can be seen in the application of a relatively high laser power that was adjusted to be well above the threshold of precursor ion formation to allow for the efficient occurrence of the aggregation processes. A continuous accelerating voltage of 20 kV was applied to the stainless steel sample holder, which accelerated all ions derived from a single laser shot into the mass analysing region of the instrument. No additional expansion or further cooling in a carrier gas was applied during the desorption/ionization process. Individual ToF mass spectra were accumulated, so that the spectra shown here represent the sum of 200 single-laser-shot spectra.

The C_{70} oxides were prepared by the method for the oxidation of C_{60} reported recently by Balch et al. [6]. C_{70} in toluene was heated to ~80°C with *m*-chloroperoxybenzoic acid (which acted as the oxidising agent) for 24 h. The separation and purification of the products was achieved by preparative high performance liquid chromatography (HPLC) after prewashing with base followed by separation and drying of the toluene layer. The multistep chromatographic separation employed both Cosmosil Buckyprep and Buckyclucher columns using toluene and/or toluene/heptane mixtures as eluants. The separated fractions were analysed subsequently by MALDI ToF mass spectrometry and a more detailed account on the derived findings will be given in a forthcoming article [23]. For the present MALDI experiments, the C_{70} oxides were kept as eluant solutions and added directly to the matrix solution containing 9-nitroanthracene dissolved in toluene. The analyte/matrix solution was deposited onto a stainless steel target slide and dried in a cold air stream before introduction into the ion source.

The negative-ion MALDI mass spectra of $C_{70}O$ and $C_{70}O_2$ are depicted in Fig. 1(a) and (b), respectively. Both spectra show the molecular ion signal of the target material as the base peak, together with fragment ion signals of lower intensity. The molecular ions are accompanied by oxide anions containing more oxygen atoms than the initial target molecule. These ions are thought to result predominately from the transfer of oxygen from the matrix to the analyte, as established by separate MALDI experiments in which pure fullerenes were found to be efficiently

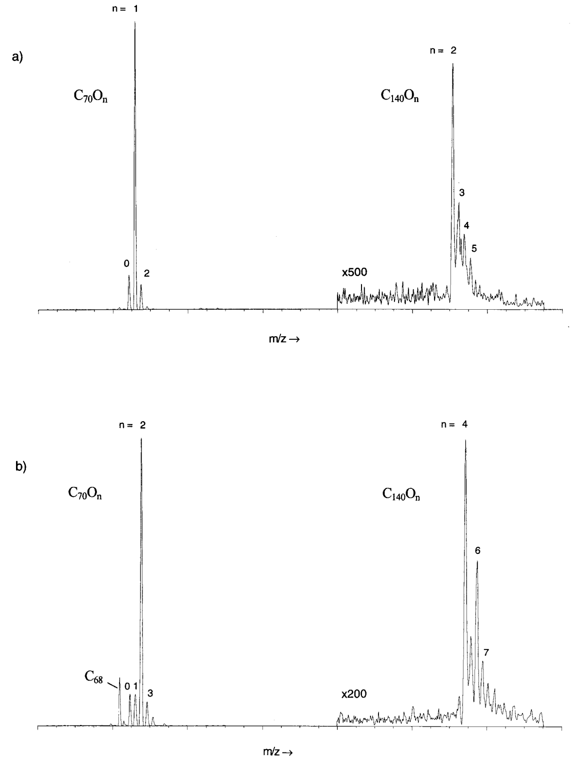

Fig. 1. (a) Negative ion MALDI mass spectrum of $C_{70}O$ embedded in 9-nitroanthracene. (b) Negative ion MALDI mass spectrum of $C_{70}O_2$ embedded in 9-nitroanthracene. Both spectra show a mass range of *m/z* 600–2000.

oxygenated applying the same conditions. At the high mass end in both spectra, the signals for the formation of $(C_{70})_2O_n$ anions are observed. The formation of the dimer results in the most intense signal followed by several species containing more oxygen atoms than initially present in the target material. Occasionally, smaller satellite peaks are also observed that formally result from CO loss from higher oxygenated aggregates. The abundance and the extent to which higher oxygenated aggregates are obtained is not as pronounced as previously observed for C_{60} oxides [19]. As to whether this observation is caused by structural features or results from a different composition of the plume cannot be answered here. Both spectra clearly show that conditions are met allowing fragmentations to occur in which the precursor oxide dissociates into a pure carbon cluster fragment ($C_{70}^{-\bullet}$ from $C_{70}O$ and $C_{68}^{-\bullet}$ from $C_{70}O_2$). The entire absence of any pure carbon cluster ions in the mass region of the aggregates is taken as strong support for their proposed structure consisting of two connected intact C_{70} moieties rather than a fused C_{140} entity. With regard to the observation of $C_{68}^{-\bullet}$ originating from $C_{70}O_2$, it is interesting to note that experiments based on mass spectrometry revealed that phenylated C_{68} can be formed readily from $C_{70}Ph_8O_4$ by the loss of $2CO_2$ [24].

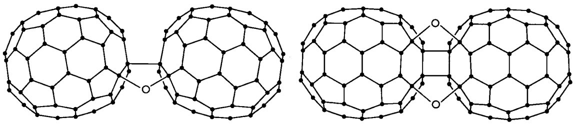

Fig. 2. Proposed core structures of the generated $C_{140}O_n$. For a detailed semi-empirical investigation into these structures see [18].

According to semiempirical calculations, the furanoid bridging represents the energetically most favourable way for the linkage of C_{60} oxides [18]. In Fig. 2 are shown two low energy $(C_{70})_2O_n$ dimers with $n = 1$ and 2, respectively, which have been described recently by a comprehensive MNDO treatment [18]. For geometrical reasons, the likelihood of encountering more than two furanoid bridges in these dimers appears rather remote, so that we assume that the structure arrangement given in Fig. 2 shows the most likely method of connection of the cores of those dimeric gas-phase aggregates, whereas additional oxygen atoms might be attached as epoxide groups. These assumptions are supported by the recent isolation and characterisation of two $C_{120}O_2$ isomers by Krätschmer and co-workers [25], where one species exhibits two neighbouring furanoid bridges and the other isomer shows only one furanoid bridge connecting C_{60} with $C_{60}O$. These considerations clearly underline that the method applied here to prepare $(C_{70})_2O_n$ might give rise to a wide variety of isomeric products, possibly even including much more weakly bound species than those incorporating the assumed furanoid-bridged core.

However, in contrast to recent unsuccessful efforts to synthesise $(C_{70})_2O_n$ in the condensed phase, it has been shown that MALDI provides a means to generate these aggregates in the gas phase.

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