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Addition of Alcohols and Hydrocarbons to Fullerenes by Photosensitized Electron Transfer

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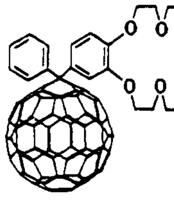
The advent of a method for the preparation of macroscopic amounts of C_{60}[1] by Krätschmer and Huffman[2] has led to a large body of literature describing the wide range of chemical reactivity of fullerenes.[3] In an initial foray into the relatively unexplored area of photochemical functionalization of fullerenes, we reported the facile [2 + 2] photocycloadditon of cyclic enones to C_{60}[4] and the isolation of enantiomeric pairs of the diastereomeric *cis*- and *trans*-fused photoadducts.[5] We now report the formation of C_{60} radical cations by photosensitized electron transfer and the capture of the cation by nucleophiles such as alcohols to yield alkoxy-substituted fullerenes. In addition, we report selective trapping of the radical cation by reactive hydrogen donors to produce alkyl-substituted fullerenes. In these studies, we have utilized the crown ether–methanofullerene **1**,[6,7] which enables us to monitor the course of reaction directly by electrospray ionization mass spectrometry (ESI-MS).[8] Electrospray analysis of functionalized **1** complexed to metal cations such as Na^+ or K^+ allows for the direct detection of fullerene products.



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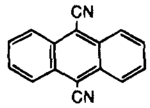

DCA

Direct laser photolysis at 425 nm[9] of a solution of methanofullerene **1** and the sensitizer 9,10-dicyanoanthracene (DCA) in toluene–acetonitrile (1:1) in the presence of excess methanol,[10] under conditions where the predominant light-absorbing species is the sensitizer,[11] yields photoproducts with a major peak at M^+ 1192, corresponding to monomethoxylation of **1**, and minor peaks at M^+ 1224, 1256, and 1288 (Figure 1), representing the di-, tri-, and tetramethoxy adducts of **1**. A similar ESI mass spectrum of a low conversion photolysate of **1** and ethanol in the presence of DCA demonstrates that ethanol also adds to compound **1**, as evidenced by major product peaks at M^+ 1206 and 1252, representing mono- and diethoxy adducts of **1**. Benzyl alcohol adds in the same manner to **1** in toluene–acetonitrile. In addition to the peak at M^+ 1268, corresponding to the alcohol–fullerene adduct, a small peak at M^+ 1252 is also observed, suggesting the formation of benzylated fullerene. The alkoxyfullerene photoadducts are all stable at room temperature under a deaerated atmosphere for at least 5 days. However, when the samples are exposed to air, the photoadducts revert back to the parent fullerene.

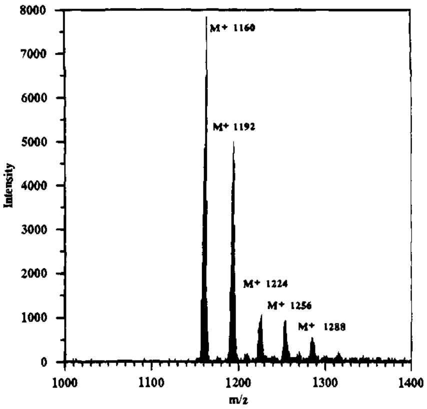

Figure 1. ESI mass spectrum of the products from the reaction of **1** with methanol sensitized by DCA in toluene/acetonitrile (1:1): M^+ 1160 (**1**−K^+); M^+ 1192 (**1**−K^+)(CH_3OH); M^+ 1224 (**1**−K^+)$(CH_3OH)_2$; M^+ 1256 (**1**−K^+)$(CH_3OH)_3$; M^+ 1288 (**1**−K^+)$(CH_3OH)_4$.

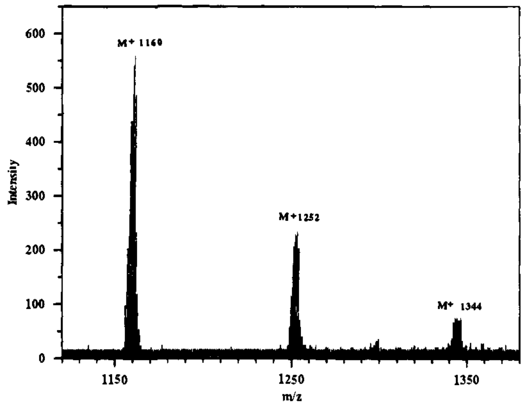

Figure 2. ESI mass spectrum of the products from the reaction of **1** with toluene sensitized by DCA in toluene/acetonitrile (1:1): M^+ 1160 (**1**−K^+); M^+ 1252 (**1**−K^+)($C_6H_5CH_3$); M^+ 1344 (**1**−K^+)$(C_6H_5CH_3)_2$.

Similar laser irradiation at 425 nm of a mixture of **1** and DCA in toluene–acetonitrile in the absence of alcohol yields major peaks at M^+ 1252 and 1344 in the ESI mass spectrum, representing mono- and dibenzylation of **1** (Figure 2). Under

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(6) Although compound **1** is depicted as a [6,6]methanofullerene, the actual sample utilized in these experiments was a 1:1 mixture of the [5,6]-expanded fulleroid and [6,6]methanofullerene.

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(9) Photons at 425 nm were generated with a XeCl excimer laser operating at 308 nm, pumping a stilbene-3 dye laser. The dye laser output was typically at 50–75 mW.

(10) In a typical experiment, an equimolar solution of fulleroid **1** and DCA (445 μM) in toluene–acetonitrile (1:1) or benzene–acetonitrile (1:1) in the presence of excess alcohol in a total sample volume of 0.5 mL was deaerated by freeze–thawing under high vacuum and irradiated with the laser at 425 nm for 10–30 min. In the alkylation experiments, the solvent was benzene–acetonitrile and the alcohol was replaced by a similar volume of hydrocarbon.

(11) At equimolar concentrations of DCA and fullerene **1** at 425 nm, the absorption of DCA is approximately 2.5 times greater than the baseline absorption of fullerene. Typically, a solution containing DCA and fullerene **1** is brown, but upon laser photolysis the sample immediately begins to glow brightly with a light bluish hue. In the absence of DCA, most of the incident light appeared to pass directly through the sample.

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similar conditions, photolysates from irradiation of **1** and DCA in the presence of cyclohexane and cyclohexene in benzene–acetonitrile solution show ESI-MS peaks at M^+ 1244 and 1242, respectively, corresponding to addition of cyclohexane and cyclohexene to **1**.

The proposed mechanism for the photosensitized addition of alcohols to fullerenes, based on the classic studies by Arnold,[12] is outlined in Scheme 1.

Scheme 1

$$\mathrm{DCA} \xrightarrow[425\ \mathrm{nm}]{h\nu} \mathrm{DCA}^* \tag{1}$$

$$\mathrm{DCA}^* + 1 \rightarrow \mathrm{DCA}^{*}\cdots 1 \tag{2}$$

$$\mathrm{DCA}^{*}\cdots 1 \rightarrow [1]^{\bullet+}\cdots[\mathrm{DCA}]^{\bullet-} \tag{3}$$

$$[1]^{\bullet+}\cdots[\mathrm{DCA}]^{\bullet-} \xrightarrow{\mathrm{CH_3CN}} [1]^{\bullet+}_{\mathrm{solv}} + [\mathrm{DCA}]^{\bullet-}_{\mathrm{solv}} \tag{4}$$

$$[1]^{\bullet+}_{\mathrm{solv}} + \mathrm{ROH} \rightarrow [1\text{-OR}]^{\bullet} + \mathrm{H}^+ \tag{5a}$$

$$[1]^{\bullet+}_{\mathrm{solv}} + \mathrm{RH} \rightarrow [1\text{-H}]^{+}_{\mathrm{solv}} + \mathrm{R}^{\bullet} \tag{5b}$$

$$[1\text{-OR}]^{\bullet} + [\mathrm{DCA}]^{\bullet-}_{\mathrm{solv}} \rightarrow [1\text{-OR}]^{\bullet\bullet(-)}_{\mathrm{solv}} + \mathrm{DCA} \tag{6a}$$

$$[1\text{-H}]^{+}_{\mathrm{solv}} + [\mathrm{DCA}]^{\bullet-}_{\mathrm{solv}} \rightarrow [1\text{-H}]^{\bullet} + \mathrm{DCA} \tag{6b}$$

$$[1\text{-OR}]^{\bullet\bullet(-)}_{\mathrm{solv}} + \mathrm{ROH} \rightarrow \text{H-1-OR} + \mathrm{RO}^- \tag{7a}$$

$$[1\text{-H}]^{\bullet} + \mathrm{R}^{\bullet} \rightarrow \text{H-1-R} \tag{7b}$$

It involves (1) initial excitation of DCA, (2) formation of an encounter complex between excited sensitizer and ground state **1**, (3) electron transfer to form a radical ion pair, (4) solvent separation of the fullerene radical cation and the DCA radical anion, (5a) attack of the alcohol on the fullerene radical cation to generate the fullerene alkoxy radical, (6a) back electron transfer from DCA radical anion to the alkoxyfullerene radical to give the alkoxyfullerene anion and neutral sensitizer, and finally (7a) protonation of the anion by alcohol to yield the neutral alkoxyfullerene. An alternative mechanism for formation of alcohol–fullerene adducts, involving initial hydrogen abstraction from the solvent (toluene) by the fullerene radical cation, followed by nucleophilic attack of the alcohol on the fullerene cation to give the alkoxylated product, can be discounted by the observation that methanol adducts of **1** are also formed on DCA photosensitization in benzene–acetonitrile solutions.

Because of the relatively large concentrations of DCA relative to the fullerene required for these experiments, to ensure that light is absorbed almost entirely by the sensitizer, fluorescence quenching studies for mechanistic proof of the proposed reaction pathway are problematic. Nevertheless, we have reasonable confidence that this mechanism is operative in our reaction, since photolysis at 425 nm of **1** in the presence of methanol in the absence of DCA yields only the starting material, as observed by ESI-MS. Although C_{60} generally behaves chemically as a mild oxidizing agent,[7b] electron transfer from compound **1** to DCA singlet excited states should be energetically favorable[13] and ought to occur at a diffusion-controlled rate to produce fullerene radical cations, based on the finding that oxidation of C_{60} in benzonitrile occurs at +1.76 V.[14]

The formation of fullerene adducts of toluene, cyclohexane, and cyclohexene when **1** and DCA are irradiated at 425 nm in the absence of a nucleophile indicates that under these conditions the fullerene radical cation (eqs 1–4 in Scheme 1) can behave as a typical free radical and abstract hydrogen from a suitable hydrogen donor, in contrast to reaction at the cationic center when alcohol is present. Nucleophilic addition is probably faster than the competitive hydrogen abstraction since only alkoxylated products are observed using methanol and ethanol in toluene–acetonitrile solvent. Hydrogen abstraction becomes competitive with nucleophilic attack on the radical cation in the case of benzyl alcohol, as evidenced by the formation of benzylated as well as alkoxylated fullerenes. The proposed mechanism for the alkylation of **1**, as outlined by Scheme 1, is as follows: after formation and solvent separation of the radical ion pairs (eqs 1–4), the fullerene radical cation abstracts a hydrogen from an appropriate donor to generate the hydrogenated fullerene cation (eq 5b), back electron transfer from DCA radical anion to the fullerene cation regenerates the fullerene radical and neutral DCA (eq 6b), and finally coupling of the fullerene radical and the alkyl radical furnishes the alkylated fullerene (eq 7b).

Although formation of alkoxy[15] and benzyl[15,16] fullerenes has been observed previously in processes which have utilized charged reagents such as $NaOCH_3$ and radical initiators, respectively, the present novel photochemical method offers possible synthetic advantages in its ease, the relative mildness of the reaction conditions, and the predominance of a monosubstituted fullerene as the major product.

Conclusion. Generation of fullerene radical cations by photosensitized electron transfer from electronically excited DCA in toluene– and benzene–acetonitrile solutions, modeled on the photosensitized nucleophilic additions to alkenes originally reported by Arnold,[12] results in addition of alcohols to fullerenes, giving principally monoalkoxy adducts. When the alcohol is replaced by an appropriate hydrogen donor, alkylated fullerene adducts are generated. Fullerene radical cations have not received much attention previously as reaction intermediates in solution. The finding that fullerene radical cations in the vapor phase are unreactive toward alcohols[17] was rationalized in terms of resistance to formation of product in which the previously highly delocalized positive charge becomes strongly localized upon the oxygen atom of the nucleophile. This inhibition is not the case in solution, probably because of solvation effects. We expect to utilize these novel reactions of fullerenes to add other types of nucleophiles (such as cyanide) and hydrogen donors (such as thiols) to C_{60}, thus opening a wider window for functionalization of fullerenes for synthetic purposes. These studies once again demonstrate the value of using the crown ether–methanofullerene **1** to conveniently follow the progress of new chemical reactions of C_{60} in solution by ESI-MS.

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