

# Detection of Methoxylated Anions of Fullerenes by Electropray Ionization Mass Spectrometry

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**Abstract:** Electropray ionization mass spectrometry (ESI-MS) has been applied to the study of the reactions of fullerenes in solution. The  $C_{60}^-$  and other anionic species are readily examined directly in 1:1 toluene/methanol by negative ion ESI-MS. Addition of a NaOMe/MeOH solution to  $C_{60}$  in toluene leads to formation of  $C_{60}^-$  and  $C_{60}(OMe)_n^-$  ( $n = 1, 3, 5, 7$ ) as major anions as well as a product derived from coupling and oxidation with toluene,  $C_{60}O_2(CH_2C_6H_5)^-$ . The expected isotopic shifts of the peaks in deuteriomethanol or deuteriotoluene confirmed the proposed formulas. Similar experiments on  $C_{70}$  gave the same types of anions. A crown ether tagged fulleroid was also used for the same reaction, but the ESI-MS study could be done in both positive and negative ion modes. Our results showed that fulleroids do have chemical properties similar to those of fullerenes themselves.

As the chemistry of  $C_{60}$  develops it becomes clear that its reactions are dominated by anions and anion radicals.<sup>1</sup>  $C_{60}$  is the most electropositive carbon compound known and is able to accept one to six electrons in low-lying empty orbitals.<sup>2</sup> A recent report described the addition of amines to  $C_{60}$  by an electron-transfer mechanism.<sup>3</sup> Nucleophilic hydroxylation of fullerenes has also been achieved by direct treatment with KOH in an organic solvent.<sup>4</sup> Although direct methoxylation of fullerenes has not been reported,<sup>5</sup> polymethoxylated  $C_{60}$  can be obtained from a polychlorinated compound via chlorine substitution with methoxide.<sup>6</sup>

We have been developing applications of electropray ionization mass spectrometry (ESI-MS)<sup>7</sup> to organic reactions<sup>8,9</sup> and applied

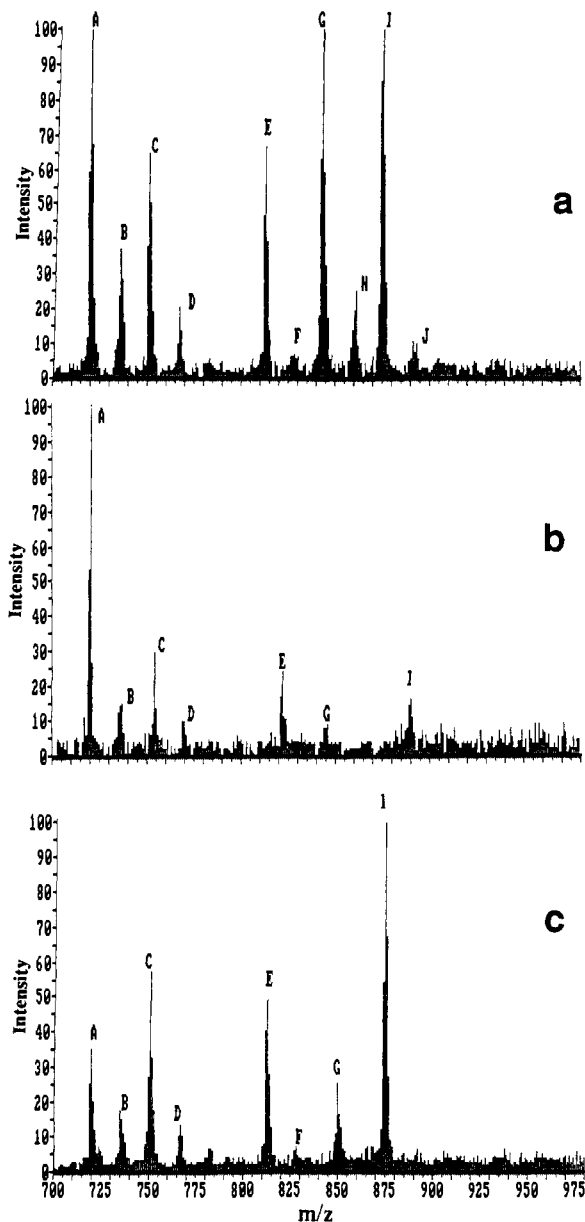
this technique to the characterization of oxyamination products of  $C_{60}$  as their ammonium salts in the positive ion mode.<sup>10a</sup> We also reported the use of a crown ether tagged fulleroid for studying reactions in solution by ESI-MS.<sup>8b,10b,c</sup> Now we report the examination of methoxide additions to  $C_{60}$  and  $C_{70}$  and the detection of fullerene anions and anionic adducts in solution by ESI-MS in both negative and positive ion mode. Recently,  $C_{60}$  and  $C_{70}$  anions have been observed by ESI-MS.<sup>11</sup>

## Results and Discussion

We have found that the addition of NaOMe/MeOH to a solution of  $C_{60}$  (1) in toluene leads to a color change from purple to brown with precipitation of unreacted  $C_{60}$ .<sup>12</sup> When the liquid phase was injected directly into the ESI-MS, the spectrum shown in Figure 1a was obtained, which shows several anionic species corresponding to the addition of odd numbers of methoxy groups! The major ions were assigned as A,  $C_{60}^-$ ; C,  $C_{60}(OMe)^-$ ; E,  $C_{60}(OMe)_3^-$ ; and I,  $C_{60}(OMe)_5^-$ . In addition, minor oxidized components were also observed (peaks B, D, F, and J). Another type of product due to addition of a benzyl group is also apparent: G,  $C_{60}O_2(CH_2C_6H_5)^-$ . To confirm the identity of the peaks, we carried out various isotopic-labeling studies. First, the structures of the methoxy-containing species producing peaks C, E, and I were examined by carrying out the reaction in  $CD_3OD/C_6H_5CH_3$  (Figure 1b). The expected shift of peaks C, E, and I by 3, 9, and 15 mass units, respectively, was observed. Confirmation of the benzylated product was obtained when the reaction was carried out in  $CH_3OH/C_6D_5CD_3$  (Figure 1c), whereupon peak G showed a shift of 7 mass units. (This experiment also established that peak G was obtained by coupling with the toluene solvent. Peak G was not observed when benzene was used as the cosolvent.) In another experiment using both  $CD_3OD$  and  $C_6D_5CD_3$ , the same spectrum as Figure 1b was obtained, except that peak G showed a shift of only 7 amu. This rules out the possibility that the species producing peak G has the formula  $C_{60}(OCH_3)(CH_2C_6H_5)^-$

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 (9) Electropray does not always provide an unbiased picture of ions in solution. The detailed mechanism for ion formation in electropray is not known and is a matter of active current research (Fenn, J. B. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 524). While ions observed in electropray often closely correspond to those present in solution, this is not always the case. Electropray response must be determined for each compound, and many factors such as type of ionic species, solvent, instrument conditions, and even source design (i.e., instrument manufacturer) affect the ions observed.

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 (12) In order to analyze the reaction mixture by ESI-MS, a high percentage of methanol is needed to maintain a stable spray current.  $C_{60}$  is very insoluble in this system, although it seems that methoxylated  $C_{60}$  anions are soluble.

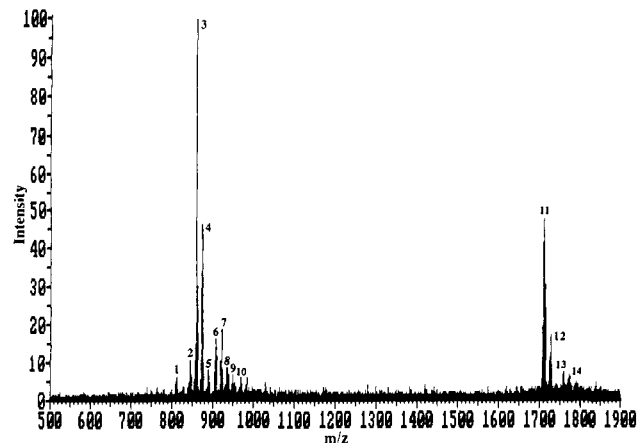


**Figure 1.** (a) Negative ion ESI-MS of the reaction of  $C_{60}$  in methanol/toluene containing  $NaOCH_3$ : A,  $C_{60}^-$  ( $m/z = 720$ ); B,  $C_{60}O^-$  (736); C,  $C_{60}(OCH_3)^-$  (751); D,  $C_{60}O(OCH_3)^-$  (767); E,  $C_{60}(OCH_3)_2^-$  (813); F,  $C_{60}O(OCH_3)_2^-$  (829); G,  $C_{60}O_2(CH_2C_6H_5)^-$  (843); H,  $C_{60}O_3(OCH_3)_3^-$  (861); I,  $C_{60}(OCH_3)_5^-$  (875); J,  $C_{60}O(OCH_3)_5^-$  (891). See Figure S1 (supplementary material) for full scan spectrum. (b) Negative ion ESI-MS of the reaction of  $C_{60}$  in  $CD_3OD$ /toluene containing  $NaOCD_3$ : A,  $C_{60}^-$  ( $m/z = 720$ ); B,  $C_{60}O^-$  (736); C,  $C_{60}(OCD_3)^-$  (754); D,  $C_{60}O(OCD_3)^-$  (770); E,  $C_{60}(OCD_3)_2^-$  (822); G,  $C_{60}O_2(CH_2C_6H_5)^-$  (843); I,  $C_{60}(OCD_3)_5^-$  (890). (c) Negative ion ESI-MS of the reaction of  $C_{60}$  in methanol/ $C_6D_5CD_3$  containing  $NaOCH_3$ : A,  $C_{60}^-$  ( $m/z = 720$ ); B,  $C_{60}O^-$  (736); C,  $C_{60}(OCH_3)^-$  (751); D,  $C_{60}O(OCH_3)^-$  (767); E,  $C_{60}(OCH_3)_2^-$  (813); F,  $C_{60}O(OCH_3)_2^-$  (829); G,  $C_{60}O_2(CD_2C_6D_5)^-$  (850); I,  $C_{60}(OCH_3)_5^-$  (875). See Figure S2 (supplementary material) for full scan spectrum.

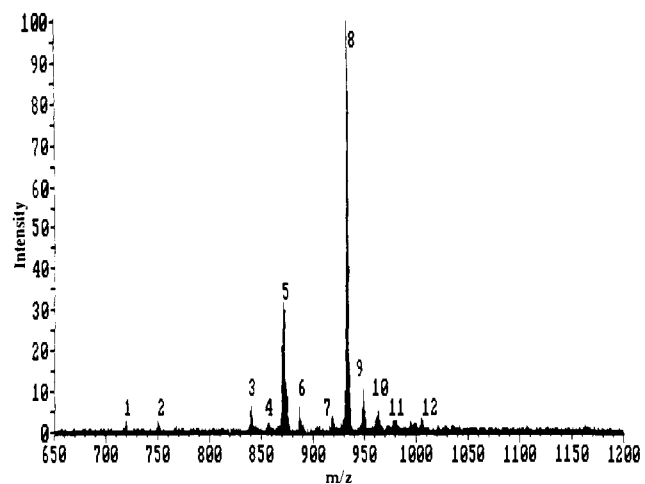
( $m/z = 842$ ), which has a very similar mass to the proposed  $C_{60}O_2(CH_2C_6H_5)^-$  ( $m/z = 843$ ).<sup>13</sup>

The expected products were also obtained if the reaction was run in the mixed solvents ethanol/toluene, methanol/benzene, or

(13) Electrospray ionization sources are most readily adapted to low-resolution quadrupole MS instruments due to design requirements for operation of an atmosphere pressure source. Low pressures and high voltages required by high-resolution magnetic sector instruments create technical difficulties (Gallagher, R. T.; Chapman, J. M. *Rapid Commun. Mass Spectrom.* 1990, 4, 369). Our Vestec ESI-MS instrument (ref 21) operates at low resolution (about 200) and therefore cannot easily distinguish isotope patterns. We believe, because of reproducibility, that we can unequivocally determine the formula within 1 amu.



**Figure 2.** Negative ion ESI-MS spectrum of the reaction mixture of  $C_{60}$  in methanol/ethylbenzene containing  $NaOMe$ . Peak assignments are 1,  $MX_3^-$  ( $m/z = 813$ ); 2,  $MO_6X^-$  (847); 3,  $MO_3X_3^-$  (861); 4,  $MX_5^-$  (875); 5,  $MOX_5^-$  (891); 6,  $MO_6X_3^-$  (909); 7,  $MO_3X_5^-$  (923); 8,  $MX_7^-$  (937); 9,  $MO_6X(CHMeC_6H_5)^-$  or  $MOX_7^-$  (953); 10,  $MO_6X_5^-$  (971); 11,  $[M_2O_4(CHMeC_6H_5)_2]^-$  (1714); 12,  $[M_2O_3X(CHMeC_6H_5)_2]^-$  (1729); 13,  $[M_2O_5X(CHMeC_6H_5)_2]^-$  (1761); 14,  $[M_2O_4X_2(CHMeC_6H_5)_2]^-$  (1776). M and X stand for  $C_{60}$  and  $CH_3O^-$  group.



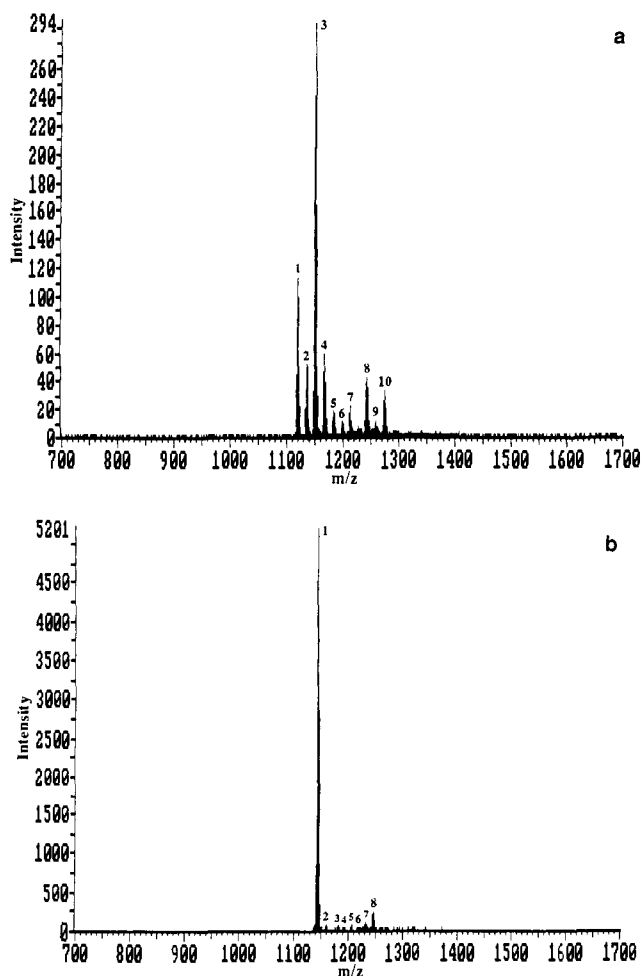
**Figure 3.** Negative ion ESI-MS of the reaction of  $C_{70}$  ( $\sim 98\%$ , Texas Fullerenes) in methanol/toluene containing  $NaOCH_3$ : 1,  $C_{60}^-$  ( $m/z = 720$ ); 2,  $C_{60}(OCH_3)^-$  (751); 3,  $C_{70}^-$  (840); 4,  $C_{70}O^-$  (856); 5,  $C_{70}(OCH_3)^-$  (871); 6,  $C_{70}O(OCH_3)^-$  (887); 7,  $C_{70}O_3(OCH_3)^-$  (919); 8,  $C_{70}(OCH_3)_3^-$  (933); 9,  $C_{70}O(OCH_3)_3^-$  (949); 10,  $C_{70}O_2(OCH_3)_3^-$  or  $C_{70}(OCH_3)_4^-$  (964-5); 11,  $C_{70}O_3(OCH_3)_3^-$  or  $C_{70}O(OCH_3)_4^-$  (980-1); 12,  $C_{60}O(OCH_3)_5^-$  (1011).

methanol/ethylbenzene.<sup>14</sup> In several cases, dimeric ions were also detected. While very small dimer peaks ( $<5\%$ ) were observed in the experiments shown in Figure 1 (cf. in the supplementary data: Figure S1, a full scan spectrum of Figure 1a, and Figure S2, a full scan spectrum of Figure 1c), quite substantial dimeric peaks ( $\sim 50\%$ ) may be seen using the solvent mixture methanol/ethylbenzene (Figure 2).

Similar methoxylation experiments were carried out on  $C_{70}$  (2), and the same type of odd-numbered methoxylated anions were observed (Figure 3). A major anion observed in this case is  $C_{70}(OCH_3)_3^-$ , although we did not follow the reaction to completion.

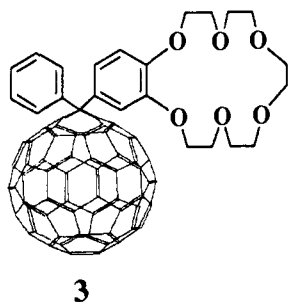
In order to gain additional insight into the apparent addition of only odd numbers of methoxy groups, we used our crown ether tagged " $C_{61}$ -fulleroid" (3)<sup>10</sup> to allow us to examine the ESI-MS in the positive ion mode. The unique feature of the crown ether

(14) Much weaker signals were detected in the experiment with ethanol, possibly because ethanol gives much worse performance in ESI-MS than does methanol. Straub, R. F.; Voyksner, R. D. *J. Am. Soc. Mass Spectrom.* 1993, 4, 578.



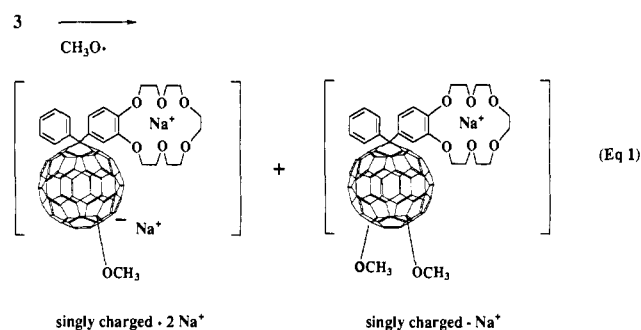
**Figure 4.** ESI-MS spectra of the reaction mixture (about 10 min after mixing) of crown ether fulleroid **3** in methanol/toluene (1:1) containing NaOMe. M and X stand for compound **3** and a  $\text{CH}_3\text{O}^-$  group. (a) Negative ion ESI-MS spectrum. Peak assignments are 1,  $\text{M}^-$  ( $m/z = 1120$ ); 2,  $\text{MO}^-$  (1136); 3,  $\text{MX}^-$  (1151); 4,  $\text{MOX}^-$  (1167); 5,  $\text{MO}_2\text{X}^-$  (1183); 6,  $\text{MO}_3\text{X}^-$  (1199); 7,  $\text{MX}_3^-$  (1213); 8,  $\text{MO}_2(\text{CH}_2\text{C}_6\text{H}_5)^-$  (1243); 9,  $\text{MO}_3(\text{CH}_2\text{C}_6\text{H}_5)^-$  (1259); 10,  $\text{MX}_5^-$  (1275). (b) Positive ion ESI-MS spectrum. Peak assignments are 1,  $\text{MNa}^+$  ( $m/z = 1143$ ); 2,  $\text{MONa}^+$  (1160); 3,  $\text{MONa}_2^+$  (1183); 4,  $\text{MOXHNa}^+$  (1191); 5,  $\text{MX}_2\text{Na}^+$  (1205); 6,  $\text{MOX}_2\text{Na}^+$  (1221); 7,  $\text{MOX}_3\text{H}_2^+$  (1231); 8,  $\text{MO}_3\text{XNa}^+$  (1245).

tagged  $\text{C}_{61}$ -fulleroid **3** is that it has chemical properties similar to those of  $\text{C}_{60}$  itself and an alkali metal binding site, so that its derivatives are "ESI active." The methoxylation reaction with the  $\text{C}_{61}$ -fulleroid **3** gave a type of anions similar to  $\text{C}_{60}$  itself.



When **3** in toluene was treated with NaOMe methanol solution, the mixture changed to cloudy and clear again in seconds ( $\text{C}_{61}$ -fulleroid **3** is much more soluble than  $\text{C}_{60}$ ). The resulting solution was used directly for ESI-MS analysis. Figure 4a,b shows the negative and positive ion ESI-MS spectra for the reaction solution right after mixing. In the negative ion mode, besides the molecular ion for **3** ( $m/z = 1120$ ), mono-, tri-, and penta-addition of methoxy

groups was again found, accompanied by minor oxygenated adducts as well as the expected product of oxidation and coupling to toluene,  $\text{MO}_2(\text{CH}_2\text{C}_6\text{H}_5)^-$  (Figure 4a). Once again, addition of only odd numbers of methoxy groups was seen, as observed previously for  $\text{C}_{60}$  in the negative ion mode. On the other hand, in the positive ion mode, unreacted crown ether fulleroid and both odd- and even-numbered methoxylated products may be observed (Figure 4b). Products from addition of odd numbers of methoxy groups show up as bis-sodium adducts, and products with even numbers of methoxy groups show up as monosodium adducts. This means that the products with even numbers of methoxy groups were *neutral* before attachment of sodium ions (eq 1).<sup>15</sup>



Deuterated reagents were again used as described above to confirm the identity of the peaks. When  $\text{NaOCD}_3/\text{CD}_3\text{OD}$  was used, the expected shift for peaks **3**, **7**, and **10** by 3, 9, and 15 mass units, respectively, was observed in the negative ion mode (Figure S3a in supplementary material). In the positive ion mode, adducts with odd- and even-numbered methoxy groups were observed, which also showed corresponding shifts (Figure S3b in supplementary material). The time course for the methoxylation reaction can also be monitored by ESI-MS. The interpretation of the negative ion spectra is much more straightforward than that of the positive ion spectra; however, both negative and positive ion spectra after 24 h showed that the penta-adducts were the major final products (Figures S4a-b in supplementary material).

Nucleophilic additions to  $\text{C}_{60}$  are known,<sup>16</sup> and several alkylated or arylated products have already been isolated and characterized.<sup>17</sup> The  $\text{C}_{60}$  monoanion has been reported to be stable in methanol and to have a  $\text{p}K_a$  estimated<sup>16a</sup> to be  $\ll 16$ , while a  $\text{p}K_a$  of 5.7 was determined for *t*- $\text{BuC}_{60}\text{H}$ , one of the strongest acids made up of only carbon and hydrogen.<sup>18</sup> Thus, it would be expected that the anionic intermediates reported herein would be stable under the experimental conditions. The observation of oxidation products of  $\text{C}_{60}$  under basic conditions has been observed previously.<sup>10,11</sup> Precedent for the formation of oxidation products of  $\text{C}_{60}$  is available from other MS studies,<sup>19</sup> and  $\text{C}_{60}\text{O}$  itself has

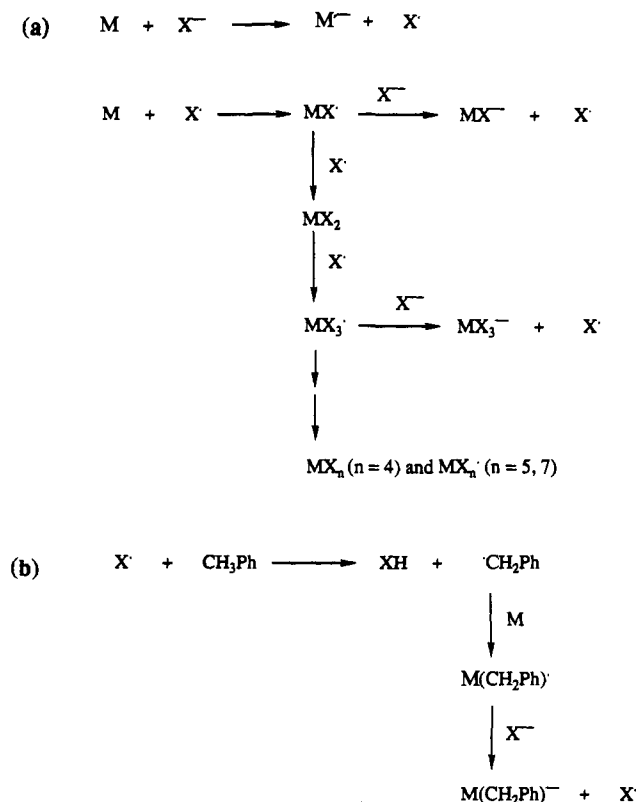
(15) The structures in eq 1 are not meant to imply that we have any evidence for the site of attachment of the methoxide substituents.

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Scheme I<sup>a</sup>

<sup>a</sup> M stands for C<sub>60</sub> (or oxygenated C<sub>60</sub>) and X for the methanol anion or radical. (a) Possible SET mechanism for addition of methoxy groups to C<sub>60</sub>. (b) Mechanism for addition of benzyl groups to C<sub>60</sub>.

been isolated and identified.<sup>20</sup> Another unusual observation from this work is also not without precedent. The detection of a benzylic adduct (peak G, Figure 1) may be related to the reports of polybenzylated products of C<sub>60</sub>.<sup>17b</sup> Dimeric C<sub>60</sub> adducts have also been isolated from the reaction of C<sub>60</sub> with *tert*-butyllithium.<sup>18</sup>

Attempts to isolate the methoxylated products were not successful. The observation of anions with only odd-numbered methoxy groups in the negative ion mode and neutral adducts with even-numbered methoxy groups in the positive ion mode may suggest a mechanism in which anion radicals are involved. A proposed mechanism is shown in Scheme I for the methoxylation of C<sub>60</sub>. This mechanism also accounts for hydrogen abstraction from toluene as well as benzyl additions. It is interesting to note that more dimers seemed to form when the toluene cosolvent was replaced by ethylbenzene (cf. Figure 2). The increased stability of the  $\alpha$ -methylbenzyl radical might favor dimerization of intermediate fullerene radicals.

## Conclusions

This work describes a new type of C<sub>60</sub> reaction as well as illustrates the capability for ESI-MS as a tool to study fullerene

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chemistry. We have demonstrated that this new technique, which has become one of the most important mass spectrometric methods for the analysis of biopolymers, also has great potential for studying organic reactions in solution. Properly designed tagged molecules can greatly facilitate the analysis as well as provide additional information. We expect that this technique will be broadly used by organic chemists and will become as useful as other routine analytical methods. Further work on the use of ESI-MS as a tool for studying C<sub>60</sub> reactions in solution is in progress and will form the basis of subsequent reports.

## Experimental Section

**General.** C<sub>60</sub> (>99%) was purchased from Strem Chemicals, Inc. C<sub>70</sub> (>98%) was purchased from Texas Fullerenes, Inc. Crown ether fulleroid 3 was synthesized as previously described.<sup>10b</sup> Toluene, deuterated toluene, deuterated methanol, benzene, and ethylbenzene were from Aldrich Chemical Company. HPLC grade methanol was from Fisher Scientific, Inc. Ethanol was from Quantum Chemical Corporation. NaOCH<sub>3</sub> and NaOCD<sub>3</sub> were prepared by dissolving sodium metal in methanol or deuterated methanol and then removing the solvent. The solids were dried under vacuum overnight. The ESI-MS measurements were performed on a Vestec Model 201 single-quadrupole electrospray ionization mass spectrometer.<sup>21</sup>

**ESI-MS Sample Preparation.** To a purple solution of C<sub>60</sub> in PhR (R = Me, Et; about 2 mg/mL) was added the same volume of a NaOMe methanol solution (40 mg/mL). The mixture turned brown with precipitation and was allowed to stand at room temperature for about 10–30 min. After filtration through a disposable pipet packed with glass wool, the light brown solution was then used directly for ESI-MS analysis.

For UV spectroscopic analysis, the reaction mixture (15  $\mu$ L) was taken right after mixing the reactants and 1 h later, after dilution with 2.5 mL of toluene/methanol (1:1). The peak for C<sub>60</sub> at 332 nm disappeared. C<sub>60</sub> itself gave two intense peaks at 281 and 332 nm under the same conditions.

In the experiments with C<sub>60</sub> in ethylbenzene or crown ether fulleroid 3 in toluene, no precipitation occurred when NaOMe/MeOH was added. The resulting brownish solutions were used directly for the ESI-MS analysis. No signal was seen when C<sub>60</sub> was treated with NaOMe in pure CH<sub>3</sub>OH or with NaOEt in pure EtOH for 3 h.

The dark brown precipitate was isolated and dried under vacuum. It did not give any signal on ESI-MS when it was redissolved in toluene/methanol (1:1). No signal was obtained from <sup>1</sup>H-NMR either. UV spectrum of this solid in toluene/methanol (1:1) showed it to be C<sub>60</sub>.

**Electrospray Ionization Mass Spectrometry.** All spectra were obtained by infusing the sample solution directly into the ESI chamber by syringe pump with the following instrumental settings: needle voltage  $\pm 2.4$  to  $\pm 2.6$  kV (+ for positive ion mode and – for negative ion mode), flow rate 5  $\mu$ L/min, needle *T* 60–63 °C, block *T* 225 °C, lens *T* 115 °C, nozzle voltage  $\pm 200$  V, repeller voltage  $\pm 20$  V. Full scan spectra (100–2000) were acquired at 13.32 s/scan to integer mass accuracy. The spectra shown represent the average of 10–15 scans.

**Supplementary Material Available:** Figures S1 and S2 containing full scan spectra of Figure 1, parts a and c, and Figures S3a,b,S4a,b, and S5a,b (10 pages). This supplementary material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the American Chemical Society. Ordering information is given on any current masthead page.

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