

# Instability of [60]fullerene anions in dichloromethane: a synthetic avenue to $C_{60} > (CH_2)_n$ methanofullerenes

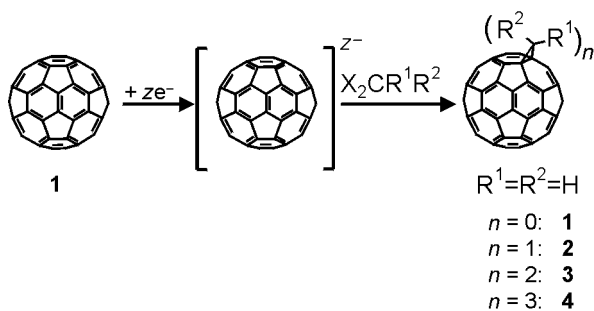
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Received (in Columbia, MO, USA) 29th December 1999, Accepted 26th April 2000

The trianion of  $C_{60}$  reacts readily with the commonly used electrochemical solvent dichloromethane to form methanofullerenes of the type  $C_{60} > (CH_2)_n$ , signaling a cautionary warning against the use of this solvent for electrochemical studies of fullerenes and opening up a new synthetic avenue for these adducts.

Since the discovery of  $C_{60}$  in 1985<sup>1</sup> and its subsequent preparation in large scale in 1990<sup>2</sup> the rich electronic properties of this fullerene have been probed by electroanalytical techniques such as cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV).<sup>3</sup> Many different experimental conditions have been used for these studies including a wide variety of supporting electrolytes and solvents (e.g. chlorobenzene, tetrahydrofuran, pyridine, nitrobenzene, *N,N*-dimethylformamide and dichloromethane).<sup>4</sup> However, a very common choice has been dichloromethane, and a very large number of fullerene derivatives have been and continue to be investigated in this solvent.<sup>5</sup> Preliminary reports identifying the instability of  $C_{60}^{3-}$  in  $CH_2Cl_2$  were published in 1991 and 1992, but no details nor product analyses were presented.<sup>6,7</sup> Since we have also performed electrochemical studies of fullerenes in  $CH_2Cl_2$  and observed quite unusual behavior<sup>8</sup> and since we published the electrosynthesis of [6,6]methanofullerenes by reacting the  $C_{60}$  monoanion and dianion with dihalomethano compounds ( $X_2CRR'$ ;  $X = Br, I$ ;  $R = H, R' = CN$  or  $CMe_3$ ),<sup>9</sup> see Scheme 1, we decided to investigate the behavior of the  $C_{60}$  anions in this solvent under bulk electrolytic conditions.



Scheme 1 Formation of methanofullerenes from the anions of  $C_{60}$ .

In a typical experiment, *ca.* 2 mg of  $C_{60}$  were suspended in dichloromethane and the anions of this fullerene were generated by controlled-potential bulk electrolysis. We followed the stability of these anions *in situ* by CV and OSWV.† The generation of the monoanion (at  $-0.85$  V vs. a Ag-wire pseudo-reference electrode) and dianion (at  $-1.25$  V) was straightforward and resulted in well defined electrochemistry [see Fig. 1(a) for the dianion]. No apparent reaction of the mono- or di-anion with the solvent was noted during or after electrolysis.<sup>10</sup> The trianion was generated by controlled potential electrolysis (CPE) applying a potential *ca.* 150 mV more cathodic than the third reduction potential of  $C_{60}$  ( $-1.60$  V). This resulted in a steady current after a few minutes, instead of the typical and expected current exponential decay observed during CPE generation of the monoanion and dianion of  $C_{60}$ , indicating that a chemical reaction occurs during electrolysis. Arbitrarily, the

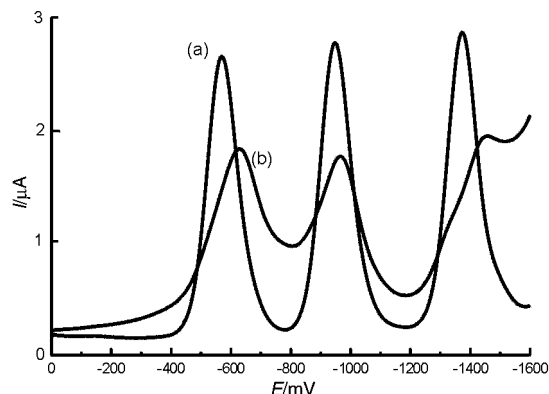


Fig. 1 OSWV of  $C_{60}$  in dichloromethane at the dianionic (a) and trianionic (b) states.

electrolysis was interrupted when *ca.* 8 electrons per  $C_{60}$  molecule were discharged (reaction time: 30 min). The OSWV was completely changed at this point [Fig. 1(b)] with the waves being much broader. Reoxidation of the reaction mixture and subsequent purification by column chromatography resulted in fullerene products in *ca.* 75% yield. Analysis of the reaction mixture by HPLC, UV–VIS spectroscopy, MALDI-TOF mass spectrometry and NMR spectroscopy showed that scarcely any  $C_{60}$  remained. UV–VIS spectroscopy showed a broad peak at *ca.* 425–435 nm while the characteristic  $C_{60}$  peak at 406 nm had disappeared. HPLC measurements [eluent hexane–toluene (10:1)] indicated the presence of several products, all slightly more polar than  $C_{60}$  itself. These products were assigned by MALDI-TOF mass spectrometric analysis (see Fig. 2), which showed the formation of several adducts of  $C_{60}$ , with  $C_{60} > (CH_2)_2$  as the main product (**1**: 2%; **2**: 20%; **3**: 50%; **4**: 15%, based on HPLC, see Scheme 1 for structure assign-

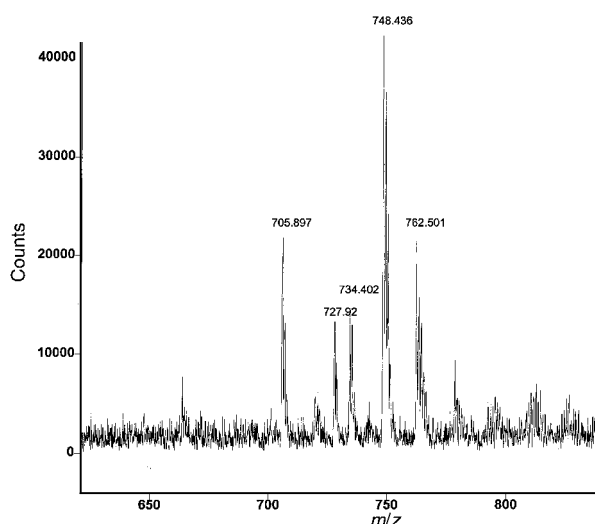


Fig. 2 Maldi-TOF spectrum of the reaction mixture after electrolysis at the trianionic state.

ments).<sup>11</sup> In practice, two different isomers can form in this reaction ([6,6] closed methanofullerenes or [5,6] open methanoannulenes).<sup>12</sup> Based on <sup>1</sup>H NMR spectroscopy, which showed several resonances (due to regioisomers of the bis- and tris-adducts) in the range  $\delta$  3.4–3.9 for the bridgehead CH<sub>2</sub>-protons, but no AB quartets at  $\delta$  2.9 and 6.4 (expected for the 5,6 isomer),<sup>12</sup> the isolated isomers were assigned to be of the [6,6] closed methanofullerene type.<sup>13</sup> Therefore, reaction of the C<sub>60</sub> trianion with the solvent dichloromethane leads to the same type of fullerene derivatives as those formed during the reaction of the C<sub>60</sub> monoanion and dianion with the diiodo and dibromo reagents previously described.<sup>9</sup> Interrupting the electrolysis at an earlier stage led to the formation of fewer adducts. A reaction time of ca. 15 min (ca. 4 electrons per C<sub>60</sub>) resulted in a product ratio of 1 : 1 of C<sub>60</sub> (**1**) to C<sub>60</sub>>CH<sub>2</sub> (**2**) (overall yield: 85%), as determined from HPLC and MALDI-TOF spectrometric measurements.

In conclusion, our experiments clearly showed that C<sub>60</sub> in its trianionic state is not stable in dichloromethane, and reacts with the solvent to form methanofullerenes. The lower reactivity of this chlorinated compound compared to the corresponding iodo and bromo compounds is compensated by its high abundance. Therefore, this solvent should be used only with extreme caution in the electrochemistry of fullerenes. Additionally, the potential application of the reaction of dichloromethane with the trianion of C<sub>60</sub> to electrosynthesize methanofullerenes with a variable number of CH<sub>2</sub> groups ranging from one to six is currently under investigation. Of special interest is the regioisomeric distribution observed, to see how it compares with that obtained from other synthetic strategies. Generally, the results described in this study and in previous work show that the anions of C<sub>60</sub> react with dihaloalkyl compounds in three different ways: the monoanion reacts with activated dihalomethano compounds [Br<sub>2</sub>CH(CN)],<sup>9b</sup> the dianion reacts with non-activated dihalomethano compounds (I<sub>2</sub>CH[CMe<sub>3</sub>]),<sup>9a</sup> and the trianion reacts with the non-activated and less reactive dihalomethano compounds (Cl<sub>2</sub>CH<sub>2</sub>).

Financial support for this work from the National Science Foundation through grant CHE-9816503, and the Netherlands Organization for Scientific Research (NWO, talent stipendium, M. W. J. B.) is greatly appreciated.

## Notes and references

† *Electrochemistry*: details of the experimental electrochemical set-up for the CV, OSWV and bulk electrolysis measurements have been described

elsewhere.<sup>14</sup> Briefly, electrochemical measurements were performed using a BAS 100W Electrochemical Analyzer (Bioanalytical systems). An electrochemical cell designed to carry out CV, OSWV and bulk electrolysis under high vacuum was used. For CV and OSWV, a glassy-carbon working electrode, a silver wire pseudo-reference electrode, and a Pt-mesh counter electrode were used. Bulk electrolysis was carried out using Pt mesh electrodes for both working and counter electrodes. As supporting electrolyte, tetrabutylammonium hexafluorophosphate was used.

*General*: UV-VIS: Shimadzu UV 2101 PC spectrometer; HPLC: Waters with a SiO<sub>2</sub> column; <sup>1</sup>H NMR: Bruker Avance-300 spectrometer; MALDI-TOF MS: PerSeptive Biosystems Voyager-DE STR spectrometer.

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- Reoxidation after electrolytically preparing the dianion of C<sub>60</sub> resulted in the isolation of mainly C<sub>60</sub> in ca. 95% yield.
- Besides the fullerenes **1–4**, some byproducts were formed. The product with *m/z* 706 was tentatively assigned to (C<sub>60</sub>CCl<sub>2</sub>-C<sub>8</sub>).
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