International Journal of Mass Spectrometry 194 (2000) 115–120

Cyano adduct anions of higher fullerenes: electrospray mass spectrometric studies

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Received 11 March 1999; accepted 20 May 1999

Abstract

Negative-ion electrospray mass spectrometry of fullerene/CN^- solutions was used to study the cyano adduct-anions of a mixture of higher fullerenes, revealing both monoanionic and dianionic species. The most abundant anions observed are $C_m(CN)^-$ and $C_m(CN)_2^{2-}$ for the higher fullerenes $m = 76, 78, 84, 86, 90, 92, 96$, and 98, which show some variation with the behaviour of C_{60} and C_{70}. In addition, some of the higher fullerenes exhibit reduced forms under the conditions of these measurements. In particular, C_{84}^-, C_{86}^-, and C_{90}^- are observed, as well as the dianions C_{84}^{2-}, C_{86}^{2-}, and C_{90}^{2-}. (Int J Mass Spectrom 194 (2000) 115–120) © 2000 Elsevier Science B.V.

Keywords: Fullerene; Fullerene adducts; Mass spectrometry; Electrospray; Negative ion

1. Introduction

Electrospray mass spectrometry (EMS) examining both positive and negative ions has been demonstrated as a powerful technique in the study of fullerenes and their adducts. The observation of C_{60} and C_{70} anions by negative-ion EMS [1], led to observation of higher fullerene anions [2]. While multiply charged anions of C_{60}, from C_{60}^{2-} up to C_{60}^{6-} have been observed by electrochemical reduction [3,4] and in alkali metal doped solid phases [5], only C_{60}^{2-} and C_{70}^{2-} have been observed by laser desorption mass spectrometry [6,7], while C_{84}^{2-} has recently been observed following electron attachment to C_{84}^- [8]. By contrast, a number of multiply-charged negative-ions of fullerene adducts have been identified. These include $C_{60}F_{48}^{2-}$ and $C_{60}F_{46}^{2-}$, formed by gas-phase electron attachment to $C_{60}F_{48}$ [9], and $C_{60}F_{46}^{2-}$ and $C_{60}F_{44}^{2-}$, formed by EMS measurement of electrochemically reduced $C_{60}F_{48}$ [10].

Negative-ion EMS has recently been extended for fullerene studies with C_{60}/CN^- and C_{70}/CN^- solutions [11–13] revealing abundant monoanionic species, namely $C_{60}(CN)_n^-$ and $C_{70}(CN)_n^-$, where $n = 1$, 3, 5, as well as dianionic species $C_{60}(CN)_n^{2-}$ and $C_{70}(CN)_n^{2-}$, where $n = 2, 4, 6$. For these experiments, 1 mM solutions in *o*-dichlorobenzene of each of C_{60} and C_{70} provided the necessary miscibility with a ~50 mM solution of NaCN in dimethylformamide. Usually 1:1 mixtures were used and examined by EMS over a period of ~1 hr after mixing. Visual observation of these solutions, originally of magenta (C_{60}) or tan (C_{70}) colour, showed an initial dark olive green shade, which changed progressively over a

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Dedicated to Professor Jim Morrison on the occasion of his 75th birthday.

PII S1387-3806(99)00122-0

period of around an hour through dirty brown variants to an earthy yellow color. In the EMS measurements early spectra are dominated by the lower mass species with the higher mass species growing with the passage of time. Monoanions generally appear before dianions with C_{70} appearing to react more slowly than C_{60}, giving rise to a relatively greater abundance of anion species which then progress at slower rates to the likely eventual neutral products. Not surprisingly the even-electron adduct-anion species indicated above are dominant, though a few odd-electron species such as $C_{60}(CN)_2^{-\cdot}$ and $C_{70}(CN)_2^{-\cdot}$ were observed. However, the $C_{60}(CN)_2^{-\cdot}$ species exhibits an isotope distribution revealing 1/2 u spacings, contrary to this formula, but suggestive of a doubly-charged ion containing two C_{60} units. The initial conjecture, that this is an ion-molecule complex, namely $C_{60}(CN)_4^{2-} \cdot C_{60}$, was later disproved by collision-induced-dissociation measurements [14], which verified it as the dimeric species $[C_{60}(CN)_2^{-\cdot}]_2$, interestingly an anion-anion dimer. The analogous $C_{60}(CN)_4^{-\cdot}$ species observed was likewise shown to exist as the anion-anion dimer $[C_{60}(CN)_4^{-\cdot}]_2$ in the electrospray environment.

2. Experimental

The solutions studied were of partly purified C_{84} (HFM4 from MER Corporation, Tucson, AZ) in benzene and *o*-dichlorobenzene as well as in mixtures of these, reacting with NaCN in dry dimethylformamide. The influence of these solvents is considerable as properties such as solubility and miscibility affect both the types and amounts of negative ions formed.

Aromatic solvents provide the highest solubilities for fullerenes, being generally higher for *o*-dichlorobenzene than benzene, though with solubilities decreasing for the higher fullerenes. Fulleride ions are observed from benzene solutions by negative-ion electrospray mass spectrometry, but only very weakly from *o*-dichlorobenzene solutions. Dimethylformamide is an appropriate solvent for NaCN, but it has poor miscibility with benzene. So a 1:1 benzene/*o*-dichlorobenzene solvent mixture for the fullerenes provides good solubility and miscibility, and with dimethylformamide is supportive of negative ion species, specifically the cyano adduct anions.

The high performance liquid chromatography (HPLC) chromatogram supplied with this fullerene mixture allows an estimate on the basis of peak areas of the relative amounts of the eleven fullerenes as C_{60} (5%), C_{70} (8%), C_{76} (6%), C_{78} (9%), C_{84} (41%), C_{86} (8%), C_{88} (5%), C_{90} (5%), C_{92} (5%), C_{94} (4%), and C_{96} (5%).

Mass spectra were obtained with, a VG BioQ triple-quadrupole system (VG Biotech, Altrincham, UK). The HFM4 solutions were of 0.8 mM based on the C_{84} mass in a 1:1 benzene/*o*-dichlorobenzene mixed solvent. A 50 mM solution of NaCN in dimethylformamide was mixed in ratios varying between 1:3 and 3:1 with the fullerene solution, which hence contained fullerene total concentrations of approximately 0.2–0.6 mM with NaCN of ~10–40 mM. Samples were passed into the spectrometer using a Rheodyne injector incorporating a 20 μL loop. The mobile phase used was propan-2-ol as recommended for its proven negative-ion sensitivity [15]. While direct injection without the use of a mobile phase was found to give similar quality spectra to loop injection, the latter was preferred as it provided for enhanced spectrometer cleanliness. It was noted though that mobile phases other than propan-2-ol resulted in poor quality spectra. A flow rate of 5 μL min^{-1} was used and all spectra were acquired in the negative-ion mode with the nozzle/skimmer (cone) voltage of 40 V. Scanning was from *m/z* 400–1250, with 12 scans being signal-averaged over a 120 s period to produce each mass spectrum. Representative spectra for the high and low *m/z* ranges obtained at different times after mixing are shown in Fig. 1.

3. Results

Spectral measurements were normally made over a period of up to 1 hr after mixing. Depending on the CN^- concentration used, prompt formation of monoanions is observed increasing in concentration with time. Dianions are formed later and increase relative to the monoanions surpassing them over a period.

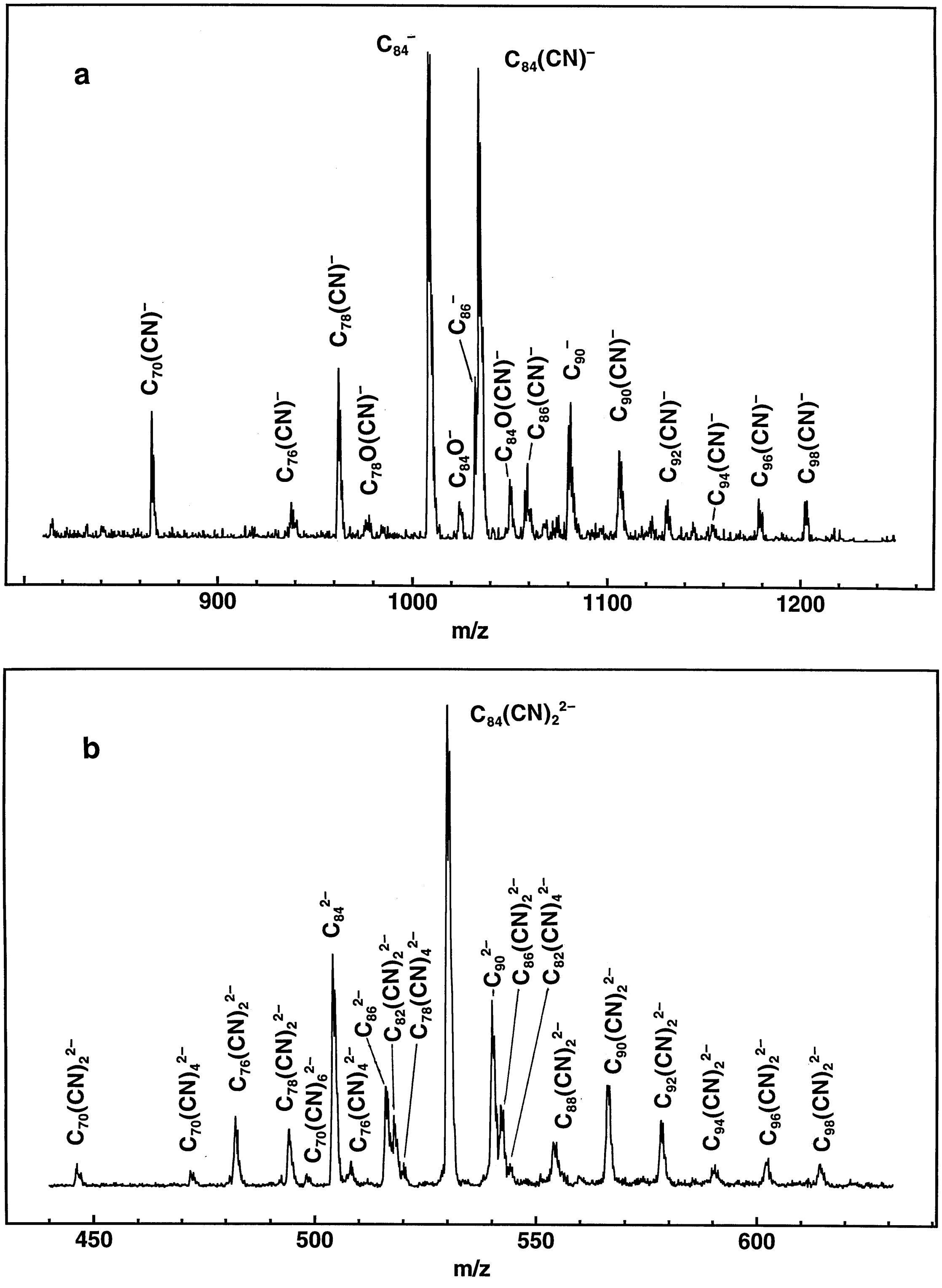

Fig. 1. Negative-ion electrospray mass spectra of higher fullerene mixture (HFM4) 0.8 mM in a 1:1 benzene/*o*-dichlorobenzene solvent mixture reacting with an equal volume of 50 mM NaCN in dimethylformamide for (a) *m/z* = 800–1250 obtained 6 min after mixing and (b) *m/z* = 440–630 obtained 20 min after mixing.

Much later there are virtually no monoanion species remaining, but dianion concentrations though reduced are still observable after 24 hr. These observations indicate that a slow addition/oxidation reaction sequence involving monoanions to dianions to neutral adducts is taking place, and that equilibria are probably achieved with a variety of species present.

Monoanion adducts

The dominant ions in the high *m/z* range are the mono-cyano adduct-anions $C_m(CN)^-$ as indicated in Fig. 1(a), for each of the higher fullerenes in the mixture. The relative peak heights show a reasonable correspondence with the percentages shown in the HPLC chromatogram. However, $C_{88}(CN)^-$ is not observed, as analysis of an expanded isotope distribution pattern for C_{90}^- starting at $m/z = 1080$ does not reveal any significant underlying presence of $C_{88}(CN)^-$ starting at $m/z = 1082$. Also $C_{98}(CN)^-$ is observed though C_{98} is not identified as present in the HFM4 sample.

An additional feature of the monoanion spectrum are the strong peaks arising from the reduced species C_{84}^-, C_{86}^-, and C_{90}^-, as well as the analogous dianions C_{84}^{2-}, C_{86}^{2-}, and C_{90}^{2-}, which appear in the low *m/z* region illustrated in Fig. 1(b). We previously discussed the preferential formation of the mono- and di-anions of C_{84} and C_{90} in a mixed solvent system of the HFM4 mixture [16]. The explanation for this selective electron attachment to these particular higher fullerenes is not obvious, as theoretical calculations on these and their neighbour C_{86} and C_{94} species show similar first and second electron affinities (EAs) for all higher fullerenes [17] consistent with similar experimental values for the first EAs [18].

Other peaks identified in the monoanion spectra include oxygen-containing species at *m/z* ratios of 978 [$C_{78}O(CN)^-$], 1024 ($C_{84}O^-$), and 1050 [$C_{84}O(CN)^-$]. As with earlier studies on C_{60} and C_{70} [11–13] these species seem to be products of reaction with dissolved O_2, and are less likely to result from fullerene oxides present in the original sample of mixed fullerenes.

Dianion adducts

The low *m/z* range spectrum shown in Fig. 1(b) is dominated by the $C_m(CN)_2^{2-}$ species for all the higher fullerenes in the mixture, as well as additional weak peaks for $C_{82}(CN)_2^{2-}$ and $C_{98}(CN)_2^{2-}$, verifying the presence of small amounts of other fullerenes, C_{82} and C_{98}, in the HFM4 sample. Again, the relative peak heights are approximately representative of the amounts of each fullerene in the sample mixture. However, there are some higher adduct species observed, specifically $C_{70}(CN)_4^{2-}$ and $C_{76}(CN)_4^{2-}$, as well as very weak peaks for $C_{70}(CN)_6^{2-}$ and $C_{76}(CN)_6^{2-}$. The absence of analogous peaks for C_{84} and C_{90} in particular indicates a further aspect of the strikingly different chemical reactivity of these higher fullerenes. Also, though $C_{88}(CN)_2^{2-}$ is observed it shows lower intensity than $C_{86}(CN)_2^{2-}$ and $C_{90}(CN)_2^{2-}$ on either side of it. The lower reactivity of C_{88} is accentuated by the effective absence of $C_{88}(CN)^-$, as indicated above, while both $C_{86}(CN)^-$ and $C_{90}(CN)^-$ are present.

4. Calculations

Semiempirical calculations based on the AM1 approximation using the MOPAC program [19] have previously been able to identify the likely preferred isomers of the $C_m(CN)_n^{z-}$ species for $m = 60, 70$, $n = 1$–6, and $z = 1, 2$ [11–13]. The higher fullerenes of the present study exhibit a greatly increased range of possible isomers for the larger cyano-adducts with $n = 2$ and greater. Here we have restricted calculations to a comparison of the monoanion ($n = 1$) species for those fullerenes of known structure, namely C_{84} with two isomers, of D_{2d} symmetry (nmr = 11) and D_2 (nmr = 21), and C_{90} with two isomers, C_2 (nmr = 45) and C_{2v} (nmr = 24), where the nmr numbers indicate the number of different types of carbons in each molecule [20]. Comparison is made with the earlier results for C_{60}, I_h (nmr = 1) and C_{70}, D_{5h} (nmr = 5) [11,13]. The data given in Table 1 are restricted to the lower energy monocyano isomers of these six fullerenes, specifi-

Table 1
MOPAC/AM1 results for selected isomers of $C_m(CN)^-$ for $m = 60, 70, 84, 90$: calculated ionization energies, IE (in eV) and standard heats of formation, ΔH_f^0, with the derived properties CN binding energies, ΔH_b^0, and relative energies, ΔH_r^0 (in kJ mol^{-1})

Molecule	Structure[a]	IE	ΔH_f^0	ΔH_b^{0b}	ΔH_r^{0b}
$C_{60}CN^-$		5.13	3817	439	
$C_{70}CN^-$	7-	5.17	4160	467	0
	21-	5.07	4162	465	2
	1-	5.13	4170	457	10
$C_{84}(D_{2d})CN^-$	32-	5.47	4557	503	0
	13-	5.29	4572	488	15
$C_{84}(D_2)CN^-$	9-	5.47	4568	493	0
	13-	5.23	4571	490	4
	28-	5.24	4572	489	5
	3-	5.28	4576	485	8
	11-	5.16	4579	482	12
	1-	5.26	4579	482	12
	29-	5.24	4580	481	12
	10-	5.34	4581	480	14
$C_{90}(C_2)CN^-$	5-	5.44	4770	510	0
	6-	5.49	4771	509	2
	11-	5.36	4782	498	13
	81-	5.28	4782	498	13
$C_{90}(C_{2v})CN^-$	33-	5.49	4786	509	0
	37-	5.43	4788	508	2
	14-	5.35	4799	496	13

[a] The numbering system used is that described in [21].

[b] ΔH_b^0 is given by $-\Delta H_f^0$ for the reaction $C_m + CN^- \rightarrow C_m(CN)^-$ and ΔH_r^0 as $\Delta H_f^0[C_m(CN)^-] - \Delta H_f^0[C_m(CN)^-]_{min}$ where min indicates the preferred structure. The additional ΔH_f^0 values used are: C_{60} 4072, C_{70} 4443, $C_{84}(D_{2d})$ 4875, $C_{84}(D_2)$ 4877, $C_{90}(C_2)$ 5096, $C_{90}(C_{2v})$ 5111, and CN^- 184 in kJ mol^{-1}.

cally for isomers of up to 15 kJ mol^{-1} higher energy than the favored isomer of each. This includes the AM1 standard heat of formation, ΔH_f^0, which by comparison with the analogous data for the fullerene itself and the CN^- anion, allows calculation of the adduct binding energy, ΔH_b^0, for each monocyano species. The energy relative to the preferred isomer, ΔH_r^0, is given, as well as the calculated ionization energy *IE*, which corresponds to the electron affinity of the neutral $C_m(CN)$ species. The carbon numbering for each fullerene corresponds to the scheme recommended by IUPAC [21].

The data reveal some quite plausible trends, such as the increasing size of fullerene providing increasing ionization energy and binding energy of the mono-cyano adduct anion. A significant result is that relatively few among the possible adduct isomers of each fullerene are competitive over a 10 kJ mol^{-1} energy range. So the known stable D_{2d} isomer of C_{84} has only one likely mono-cyano adduct, the 32- species, while the stable C_2 isomer of C_{90} has only two likely mono-cyano adducts, the 5- and 6- species.

5. Discussion

It is interesting to compare these observations for the higher fullerenes with the results obtained earlier for C_{60} and C_{70} [11–13]. An interesting comparative observation for the higher fullerene/CN^- solutions concerns the apparent stability of their negative ions, which are maintained for longer periods in comparison with those of the smaller homologs C_{60} and C_{70}. They appear to show rather faster conversion of monoanions to dianions but much slower evolution to the ultimate neutral adduct species. While quantitative kinetic studies on these reactions would be worthwhile, these will be better undertaken when pure samples of representative higher fullerenes become available.

A surprising aspect of the measured spectra is the absence of larger monoanion adducts $C_m(CN)_n^-$ with $n = 3, 5$, as previously observed under similar conditions for C_{60} and C_{70} [11,13]. The above observation that the higher fullerenes exhibit higher rates of dianion adduct formation than C_{60} and C_{70} may explain the absence of such larger monoanion adducts. Analogously, the larger dianion adducts $C_m(CN)_n^{2-}$ with $n = 4, 6$ observed for C_{60} and C_{70} [12,13] are only represented by small amounts of $C_{76}(CN)_4^{2-}$ and $C_{76}(CN)_6^{2-}$ among the higher fullerenes.

6. Conclusion

Anionic species observed in the negative-ion electrospray mass spectrometry of higher fullerene/CN^- solutions include monoanionic and dianionic species. The most abundant cyano-anions are the mono- and di-adducts $C_m(CN)^-$ and $C_m(CN)_2^{2-}$ observed for most fullerenes, while fulleride species C_m^- and C_m^{2-} are observed for only $m = 84$, 86, and 90. In comparison with the widely-studied C_{60} and C_{70}, and among themselves, the higher fullerenes show interestingly different chemical reactivities which are clearly worthy of further study.

Acknowledgements

The authors thank J.C. Traeger and I.M. Thomas for assistance with the EMS measurements, and La Trobe University for an Australian Postgraduate Award to G.K.

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