Cyano Adduct Anions of C_{70}: Electrospray Mass Spectrometric Studies

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Negative-ion electrospray mass spectrometry of C_{70}/CN^- solutions was used to study the cyano adduct anions of [70]fullerene, revealing both monoanionic and dianionic species. The most abundant anions are $C_{70}(CN)_n^-$, $n = 1, 2, 3$, and $C_{70}(CN)_n^{2-}$, $n = 2, 4, 6$, with $C_{70}(CN)^-$ as the dominant anion at low concentrations. The observation of $C_{70}(CN)_2^{\bullet-}$, the only odd-electron species identified, is at variance with the behavior of C_{60} where only even-electron anions were observed under similar experimental conditions. Semiempirical calculations suggest that CN addition is generally favored in the unique "equatorial" region of C_{70} and that in the dianion species this region is able to support two negative charges in relative proximity, in contrast to the results obtained for C_{60} dianion adducts.

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] Among simple adduct species the methoxylated anions of C_{60} and C_{70} have been revealed by negative-ion EMS.[2,3] While multiply charged anions of C_{60}, from C_{60}^{2-} up to C_{60}^{6-} have been observed by electrochemical reduction [4] and in alkali-metal-doped solid phases,[5] only a few 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 $C_{60}F_{48}$,[6] and $C_{60}F_{46}^{2-}$ and $C_{60}F_{44}^{2-}$ by EMS measurement of electrochemically reduced $C_{60}F_{48}$.[7]

Negative-ion EMS has recently been extended for fullerene studies with C_{60}/CN^- solutions[8] revealing three abundant monoanionic species, namely, $C_{60}(CN)_n^-$, $n = 1, 3, 5$, with $C_{60}(CN)^-$ as the dominant anion in agreement with the observations by Wudl and co-workers.[9] Additionally three dianions of cyano-adducted buckminsterfullerene, $C_{60}(CN)_n^{2-}$, $n = 2, 4, 6$, were also observed.[10] In these experiments only the even-electron adduct-anion species were dominant, even though the mechanisms involved in their formation must include steps involving electron-loss (oxidation) as well as CN^- addition. Consequently odd-electron species such as $C_{60}(CN)_2^{\bullet-}$ are likely to be formed but clearly have relatively short lifetimes under the conditions of the experiments.

In the case of the methoxylated anions of C_{60}, different EMS spectra were obtained by Wilson and Wu[3] and by Hiraoka and co-workers.[2] The former observed only the even-electron species, $C_{60}(OMe)_n^-$, $n = 1, 3, 5$, which are the more likely long-lived anions in solution, as confirmed by semiempirical theoretical studies.[11] By contrast the latter workers observed one odd-electron species, $C_{60}(OMe)_2^{\bullet-}$, as well.[2] It is possible that this ion results from collision-induced dissociation of the stable higher ions within the electrospray source. However an electrospray source can also behave as an electrochemical cell,[12,13] and since C_{60}^- is observed in the EMS of C_{60} solutions,[13] analogous reduction of $C_{60}(OMe)_2$ would produce $C_{60}(OMe)_2^{\bullet-}$. In the observed EMS spectra for C_{60}/CN^- solutions a peak corresponding to the odd-electron $C_{60}(CN)_2^{\bullet-}$ species was observed,[8] but this showed an isotope distribution revealing $^1/_2$ amu spacings, contrary to this formula. This was interpreted as arising from a doubly charged ion containing two C_{60} units, specifically the ion−molecule complex $C_{60}(CN)_4^{2-}{\cdot}C_{60}$. Since free $C_{60}(CN)_4^{2-}$ is also present in the C_{60}/CN^- solutions,[10] this is not a surprising observation. In a similar fashion an analogous $C_{60}(CN)_8^{2-}{\cdot}C_{60}$ species was also observed.

2. Experimental Section

In extending these experiments to other fullerenes we have used the reaction of C_{70} (MER Corp.) in dry 1,2-dichlorobenzene with NaCN in dry dimethylformamide to provide various solutions for examination by EMS. Mass spectra were obtained with a VG BioQ triple-quadrupole system (VG Biotech, Altrincham, UK). The freshly prepared solutions, which contained C_{70} total concentrations of $\approx$0.5 mM and NaCN of $\approx$5−100 mM, were injected directly into the spectrometer using a rheodyne injector incorporating a 50 μL loop. The mobile phase used was 1:1 propan-2-ol/water as recommended for its proven negative-ion sensitivity.[14] A flow rate of 5 μL min^{-1} was used, and spectra were acquired in the negative-ion mode with the nozzle/skimmer (cone) voltage of 40 V. Scanning was from m/z 300−1000, with 25 scans being signal-averaged over a 120 s period to produce each mass spectrum.

Visual observation of typical C_{70}/CN^- solutions showed an initial olive green color that changed progressively over a period of around an hour through dirty brown shades to an earthy yellow color. The EMS data presented here were obtained for solutions up to 2 h following preparation. Representative spectra measured at different times are shown in Figure 1. These exhibit strong peaks around m/z values of 450 (dianion region) and 850 (monoanion region). The early spectra are dominated by the lower mass species within each range with the higher mass species growing with the passage of time. An interesting comparison with the $C_{60}(CN)^-$ observations[8,10] is that C_{70} appears 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.

3. Results

Monoanion Adducts. The three peaks located at m/z values of 866, 892, and 918 indicate the presence of the cyano adduct anions $C_{70}(CN)_n^-$, $n = 1, 2, 3$. At higher resolution the $n = 1$ and 2 peaks clearly demonstrate the appropriate isotope ratios

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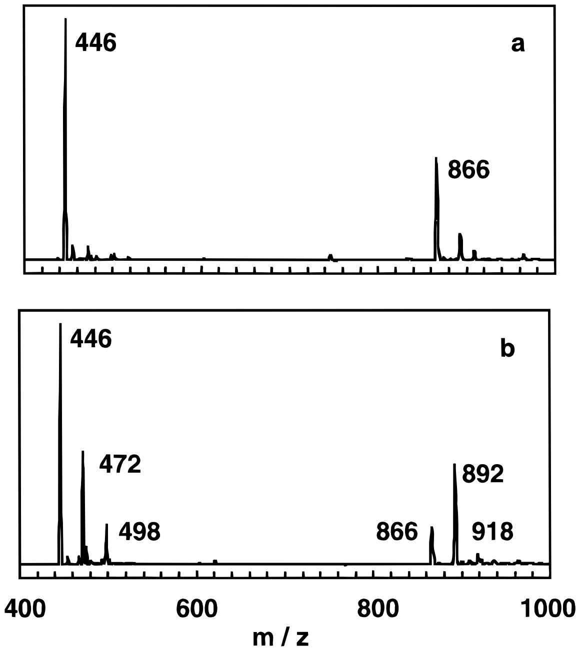


Figure 1. Negative-ion electrospray mass spectra for $m/z = 400-1000$ of C_{70}/CN^- solutions (a) $[CN^-] \approx 50$ mM at 8 min and (b) $[CN^-] \approx 50$ mM at 110 min.

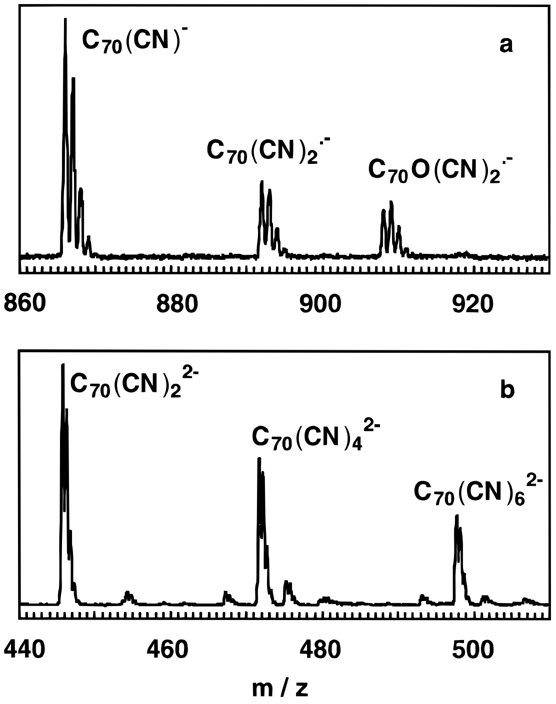


Figure 2. Comparison of experimental $^{12}C/^{13}C$ isotope distributions for the negative-ion mass spectra of (a) $C_{70}(CN)^-$ and $C_{70}(CN)_2^{\bullet-}$ and (b) $C_{70}(CN)_n^{2-}$, $n = 2, 4, 6$.

based on natural $^{12}C/^{13}C$ as illustrated in Figure 2a. The four discernible isotopes of $C_{70}(CN)^-$, of masses 866, 867, 868, and 869, have theoretical relative abundances of 100:80:31:8. Analogously the 892 peak demonstrates an isotope ratio close to the theoretical value of 100:81:32:8. However $C_{70}(CN)_2^{\bullet-}$ is an odd-electron species (the only one observed in the present study) which is at variance with the observations for C_{60}/CN^- where $C_{60}(CN)_2^{\bullet-}$ was not observed.[8] The analogue of the $C_{60}(CN)_4^{2-}\bullet C_{60}$ complex identified for C_{60}/CN^- is not seen for C_{70}/CN^- as there are no $^1/_2$ amu spacings for this 892 pattern. A further difference is that $C_{60}(CN)_5^-$ is observed in the C_{60} case but $C_{70}(CN)_5^-$ does not appear in the C_{70}/CN^- mixtures.

Figure 2a also shows an isotope pattern with discernible peaks at 908, 909, 910, and 911, with the 1 amu spacings indicating a structure based on one C_{70} unit. An m/z of 908 corresponds to an oxidized product, namely $C_{70}O(CN)_2^{\bullet-}$, but the isotope ratio is not completely consistent with this formula, so a combination with another species is indicated. In the case of the C_{60}/CN^- solutions two weaker secondary peaks were observed in the dianion spectra[10] and were assigned as arising from the species $C_{60}(CN)_5(OH)^{2-}$ and $C_{60}O(CN)_5(OH)^{2-}$. Allowing for the possibility of hydroxy as well as oxo species leads to a consideration of $C_{70}(CN)_2(OH)^-$ which would contribute an isotope pattern commencing at an m/z of 909 amu. Consequently the observed isotope pattern can be reproduced theoretically as a combination of 72% of $C_{70}O(CN)_2^{\bullet-}$ and 28% of $C_{70}(CN)_2(OH)^-$.

Dianion Adducts. The high-resolution later spectrum shown in Figure 2b exhibits abundant anions in the m/z range above 440 amu. The three strong peaks located at m/z values of 446, 472, and 498 exhibit clear $^1/_2$ amu spacings indicating the presence of the three cyano adduct dianions $C_{70}(CN)_2^{2-}$, $C_{70}(CN)_4^{2-}$, and $C_{70}(CN)_6^{2-}$. For example the four discernible isotopes of $C_{70}(CN)_4^{2-}$, of masses 892, 893, 894, and 895, have theoretical relative abundances, based on the natural ^{12}C /^{13}C ratios, of 100:81:32:8 for their respective m/z values.

There are several less abundant dianions discernible in the spectrum of Figure 2b, those with the clearest interpretable isotope patterns being the hydroxy-substituted species $C_{70}(CN)_3(OH)^{2-}$ and $C_{70}(CN)_5(OH)^{2-}$, as well as the oxo adducts of these, namely, $C_{70}O(CN)_3(OH)^{2-}$ and $C_{70}O(CN)_5(OH)^{2-}$.

4. Calculations

The results of semiempirical calculations obtained using the AM1 approximation with the MOPAC program[15] are presented in Table 1. On the basis of earlier calculations on the $C_{60}(CN)_n^-$ and $C_{60}(CN)_n^{2-}$ adducts,[8,10] the preferred isomers for the $C_{70}(CN)_n^-$ and $C_{70}(CN)_n^{2-}$ ($n \geq 2$) species are likely to be confined to relatively few within each set. The isomers listed in Table 1 are chosen from among a representative but not exhaustive selection of the probable isomers of each formula. A numbering scheme is required to precisely identify each isomer, and while a convenient geometric system has been used for the calculations, the results are presented using a previously adopted scheme.[16] The data listed for each structure include the ionization energy (Koopmans approximation), the standard heat of formation, and the mean binding energy per CN (relative to C_{70} and CN^- reactants). The latter parameters offer a simple quantitative comparison of relative stabilities of the respective sets of neutral, monoanion and dianion species. Apart from the radical anion species $C_{70}^{\bullet-}$ and $C_{70}(CN)_2^{\bullet-}$, all the species considered are even-electron systems. Within each of the (charge) classes the trends in the calculated parameters are generally the same. With increasing n, ionization energies and heats of formation increase, but mean binding energies decrease.

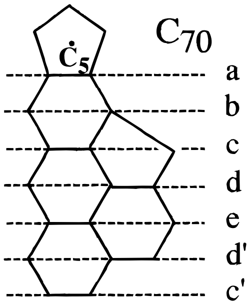
Theoretical studies of C_{70} adducts are relatively rare and, in comparison with C_{60}, are complicated by the presence of five different carbon types. These are labeled as **a**−**e** in the original NMR assignment, and are illustrated in the sectional structure of C_{70}, with the **a** carbons spanning the "polar" regions (identified by the C_5 symmetry axis) and the **e** carbons located on the "equator" of the oblate spheroidal system. Primes denote the carbons **d′**, **c′**, **b′**, **a′** in the other "hemisphere".

This structure illustrates the two different types of pentagon and the three different types of hexagon in C_{70}. Hence there are five possible isomers of $C_{70}(CN)^-$ for which Table 1 indicates the favored adduct site as the **c** carbon followed closely

TABLE 1: MOPAC/AM1 Results for Selected Isomers of $C_{70}(CN)_n$, $n = 2, 4, 6$, $C_{70}(CN)_n^-$, $n = 1, 2, 3$ and $C_{70}(CN)_n^{2-}$, $n = 2, 4, 6$: Calculated Ionization Energies, IE (in eV) and Heats of Formation, ΔH_f, with Mean Binding Energies Per CN, ΔH_b (in kJ mol^{-1})

molecule	structure[a]		IE	ΔH_f	ΔH_b[b]
C_{70}			9.14	4443	
$C_{70}^{\bullet -}$			3.81	4103	
CN^-			3.13	184	
$C_{70}CN^-$	1	(a)	5.13	4170	457
	6	(b)	5.04	4186	442
	7	(c)	5.17	4160	467
	21	(d)	5.07	4163	465
	23	(e)	5.10	4243	385
$C_{70}(CN)_2$	1,9	(ab)	9.16	4626	93
	7,8	(cc)	9.33	4624	94
	1,7	(ac)	9.34	4623	94
	21,42	(dd′)	9.32	4622	95
$C_{70}(CN)_2^{\bullet -}$	1,9	(ab)	3.93	4273	269
	7,8	(cc)	4.04	4266	273
	1,7	(ac)	4.26	4250	281
	21,42	(dd′)	3.71	4277	267
$C_{70}(CN)_2^{2-}$	1,7	(ac)	1.75	4126	343
	21,42	(dd′)	1.53	4157	327
	7,47	(cc′)	2.38	4139	336
	21,38	(dd)	2.22	4108	352
$C_{70}(CN)_3^-$	6,9,12	(bbb)	5.46	4320	225
	21,38,42	(ddd′)	5.29	4299	232
$C_{70}(CN)_4$	6,9,12,15	(bbbb)	9.08	4803	94
	21,38,42,57	(dd′d′d)	9.46	4774	102
$C_{70}(CN)_4^{2-}$	6,9,12,15	(bbbb)	1.94	4285	224
	21,38,42,57	(dd′d′d)	1.72	4278	226
	21,38,42,45	(ddd′d′)	2.65	4223	239
	6,9,12,70	(bbba′)	2.68	4260	230
	21,38,42,50	(ddd′d)	2.68	4246	234
$C_{70}(CN)_5^-$	6,9,12,15,18	(bbbbb)	6.11	4416	190
	21,26,38,42,45	(ddd′d′d)	5.44	4439	185
$C_{70}(CN)_6$	1,6,9,12,15,18	(abbbbb)	9.21	4946	100
	21,26,38,42,45	(dd′d′ddd′)	9.55	4927	103
$C_{70}(CN)_6^{2-}$	1,6,9,12,15,18	(abbbbb)	1.99	4420	188
	6,9,12,15,18,60	(bbbbbc′)	3.12	4328	203
	6,9,12,15,18,70	(bbbbba′)	3.09	4333	203
	21,26,38,42,45,57	(dd′d′ddd′)	1.88	4404	191
	21,26,29,38,42,45	(ddd′d′dd)	2.46	4365	197

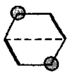
[a] The numbering system used is that given in ref 16. The lettering scheme for carbons **a**, **b**, **c**, **d**, **e**, **d′** is explained in the text. [b] ΔH_b is given by $-\Delta H/n$ for the reaction $C_{70} + nCN^- \rightarrow C_{70}(CN)_n/C_{70}(CN)_n^-/C_{70}(CN)_n^{2-}$.



by the **d** carbon. An analysis of the charge distribution of each $C_{70}(CN)^-$ shows that the negative charge is located mostly on and near the CN group, principally on the carbon atoms in the 2 and 4 positions. So for the higher monoanion species structures with reasonably localized CN groups should adequately support the excess negative charge in their vicinity.

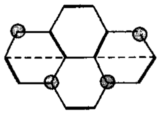
The preferred isomers of the neutral species are structurally similar to those for the C_{60} molecule, being based on competition between 1,2 and 1,4 additions with the poly-adducted species preferring "strings" of 1,4 additions. The essential variation for C_{70} is that there is the additional competition between the unique "equatorial" region and the "polar" region (common with C_{60}), with the former generally being the preferred site for addition. While the listed $C_{70}(CN)_2$ isomers are of similar stability, there is a clear theoretical preference shown for "equatorial" addition in $C_{70}(CN)_4$ (**dd′d′d**) and $C_{70}(CN)_6$ (**dd′d′ddd′**). In their minimum energy structures illustrated below, the dashed line joins the "equatorial" carbon atoms.

$C_{70}(CN)_2$



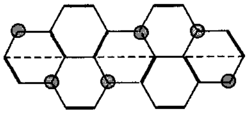
dd'

$C_{70}(CN)_4$



dd'd'd

$C_{70}(CN)_6$

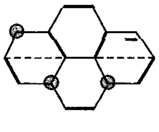


dd'd'ddd'

The addition of one negative charge for each monoanion should not greatly vary these influences and the preferred isomers are expected to have related structures. The odd-electron species $C_{60}(CN)_2^{\bullet -}$ shows a preference for the (**ac**) structure, though its IE (4.26 eV) is only slightly less than either of the adjacent $C_{70}(CN)^-$ (5.17 eV) and $C_{70}(CN)_3^-$ (5.29 eV) species. This gives one indication as to why this species is stable in the C_{70}/CN^- mixtures.

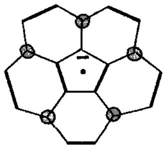
For $C_{70}(CN)_3^-$ an "equatorial" 1,4- string (**dd′d′**) is preferred with the negative charge effectively localized on an adjacent adduct site. However $C_{70}(CN)_5^-$ is an exception with the "polar" region (denoted in the structure diagram by a dot representing the C_5 symmetry axis) being preferred over the "equatorial" region. This is undoubtedly due to the high stability of the "crown" structure represented by the closed string (**bbbbb**) which produces a cyclopentadienide anion core as found for $C_{60}(OMe)_5^-$.[11]

$C_{70}(CN)_3^-$



dd'd'

$C_{70}(CN)_5^-$

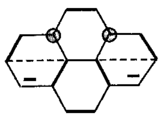


bbbbb

For the dianions the effect of charge localization is expected to have a more dramatic effect on the preferred isomer structures. This occurs for the $C_{60}(CN)_n^{2-}$ species where the repulsion between the negative charges results in a maximum physical separation of two localized $(CN)_x^-$ (odd x) groups each corresponding to the analogous monoanion structure.[10] Hence the preferred isomer of $C_{60}(CN)_2^{2-}$ is of two CN^- adducts located on opposing carbons, the 1,60 structure, with the AM1 calculations showing this to be favored by 46 kJ mol^{-1} over the 1,4 isomer.

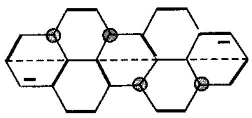
However, in the $C_{70}(CN)_n^{2-}$ species there is a surprisingly different theoretical result based on the unique properties of the "equatorial" region of C_{70} which is able to support the two negative charges in relative proximity. So $C_{70}(CN)_2^{2-}$ prefers a structure based on a 1,4 addition involving adjacent **d** carbons on the same side of the "equator", written as (**dd**). The AM1 results show a stabilization of 18 kJ mol^{-1} for this isomer relative to the nearest other 1,4-type adduct, the (**ac**) structure. However, the most stable of the structures with well-separated CN^- groups, the (**cc′**) isomer, is more energetic by 31 kJ mol^{-1} than the (**dd**) structure. While this (**dd**) structure appears to be radically different from the 1,4 (**dd′**) structure of $C_{70}(CN)_2$, it can be seen to be an extension of the relationship described above for $C_{70}(CN)_4$ and $C_{70}(CN)_3^-$, with the two charges in $C_{70}(CN)_2^{2-}$ effectively occupying the adjacent (terminal) adduct sites in a double 1,4 string. This representation is somewhat simplistic as a detailed analysis of the calculated charge distribution for the (**dd**) structure shows delocalization of negative charge around the "equatorial" region mostly involving **d** and **d′** carbon atoms. By comparison, a similar analysis for the 1,4 isomer of $C_{60}(CN)_2^{2-}$ indicates that the negative charge, though delocalized, is relatively confined to the "crown" region in which the CN^- groups are located.

$C_{70}(CN)_2^{2-}$



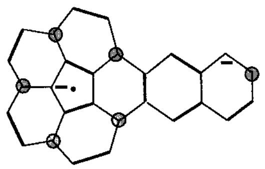
dd

$C_{70}(CN)_4^{2-}$



ddd'd'

$C_{70}(CN)_6^{2-}$



bbbbbc'

The favored structure for $C_{70}(CN)_4^{2-}$ also follows this rule and involves a (**ddd′d′**) structure with the negative charges concentrated in the **d′** and **d** positions beyond each terminal CN of the "equatorial string". However $C_{70}(CN)_6^{2-}$ does not follow analogously but has a preferred isomer influenced by the "crown" structure of $C_{70}(CN)_5^-$ as discussed above. There are two low-energy isomers which follow this pattern, as observed for $C_{60}(CN)_n^{2-}$, with well-separated $(CN)_5^-$ and CN^- groups giving a (**bbbbbc′**) configuration slightly more stable than a (**bbbbba′**) arrangement.

5. Discussion

A comparison of the spectra obtained over the time scale of the measurements indicates that simple addition steps are the basis of the mechanism of formation of the anion species observed. At low CN^- concentrations the spectra show virtually only $C_{70}(CN)^-$ present with a small amount of $C_{70}(CN)_2^{\bullet-}$ and only miniscule amounts of the lighter dianions. For higher CN^- concentrations the $C_{70}(CN)_2^{2-}$ accumulates strongly with diminishing $C_{70}(CN)^-$ and continues to be the dominant anion while there is gradual increase in the heavier dianions. The $C_{70}(CN)_2^{\bullet-}$ becomes the most prolific monoanion at later times, but only a small proportion of $C_{70}(CN)_3^-$ is produced. There appear to be larger amounts of dianions than monoanions present in the older solutions, consistent with the AM1 results which are favorable toward CN^- addition to each monoanion. No triply charged anions are observed, consistent with their calculated IEs being of negative sign as found for selected isomers of $C_{70}(CN)_3^{3-}$, indicating instability toward spontaneous electron loss.

While the semiempirical calculations indicate that all the anion species considered have sizable IEs, they are all susceptible to electron loss, possibly via electron transfer involving Na^+ on the basis of the higher IE of Na and the ability of neutral Na to be supported in the organic solvent system used, or alternately via the propan-2-ol/water mobile phase releasing OH^- ions. So a mechanistic scheme can be devised as follows:

CN^- addition

$$C_{70} + CN^- \rightarrow C_{70}(CN)^-$$

$$C_{70}(CN)^- + CN^- \rightarrow C_{70}(CN)_2^{2-}$$

$$C_{70}(CN)_2^{2-} + CN^- \rightarrow \{C_{70}(CN)_3^{3-}\}$$

electron loss (oxidation)

$$C_{70}(CN)_2^{2-} + Na^+ \rightarrow C_{70}(CN)_2^{\bullet-} + Na$$

$$C_{70}(CN)_2^{\bullet-} + Na^+ \rightarrow [C_{70}(CN)_2] + Na$$

CN^- addition

$$[C_{70}(CN)_2] + CN^- \rightarrow C_{70}(CN)_3^-$$

$$C_{70}(CN)_3^- + CN^- \rightarrow C_{70}(CN)_4^{2-}$$

electron loss (oxidation)

$$C_{70}(CN)_4^{2-} + Na^+ \rightarrow \{C_{70}(CN)_4^{\bullet-}\} + Na$$

$$\{C_{70}(CN)_4^{\bullet-}\} + Na^+ \rightarrow [C_{70}(CN)_4] + Na$$

CN^- addition

$$[C_{70}(CN)_4] + CN^- \rightarrow \{C_{70}(CN)_5^-\}$$

$$\{C_{70}(CN)_5^-\} + CN^- \rightarrow C_{70}(CN)_6^{2-}$$

Here the unobserved neutral molecules are enclosed in [ ] and the unobserved, presumably more highly reactive, anions are enclosed in { }.

Conclusions

Anionic species observed in the negative-ion electrospray mass spectrometry of C_{70}/CN^- solutions include monoanionic and dianionic (but no trianionic) species. The most abundant anions are $C_{70}(CN)^-$ at low CN^- concentrations and $C_{70}(CN)_2^{2-}$ at higher concentrations. The surprising stability of $C_{70}(CN)_2^{\bullet-}$, the only odd-electron species identified, is at variance with the behavior of C_{60} where only even-electron anions were observed under similar experimental conditions. Semiempirical calculations suggest that CN^- addition is generally favored in the unique "equatorial" region of C_{70} and that in the dianion species this region is able to support two negative charges in relative proximity, in contrast to the results obtained for C_{60} dianion adducts.

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References and Notes

(1) Hiraoka, K.; Kudaka, I.; Fujimaki, S.; Shinohara, H. *Rapid Commun. Mass Spectrom.* **1991**, *6*, 254.

(2) Fujimaki, S.; Kudaka, I.; Sato, T.; Hiraoka, K.; Shinohara, H ; Saito, Y.; Nojima, K. *Rapid Commun. Mass Spectrom,* **1993**, *7*, 1077.

(3) Wilson, S. R.; Wu, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10334.

(4) (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, *10* , 781.

(5) Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127.

(6) Jin, C.; Hettich, R. L.; Compton, R. N.; Tuinman, A.; Derecskei-Kovacs, A.; Marynick D. S.; Dunlap, B. I. *Phys. Rev. Lett.* **1994**, *73,* 2821.

(7) Zhou, F.; Van Berkel, G. J.; Donovan, B. T. *J. Am. Chem. Soc.* **1994**, *116*, 5485.

(8) Khairallah, G.; Peel, J. B. *J. Chem. Soc., Chem. Commun.* **1997**, 253.

(9) Majid, K.-K.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371.

(10) Khairallah, G.; Peel, J. B. *Chem. Phys. Lett.* **1997**, *268*, 218.

(11) Peel, J. B. *Aust. J. Phys.* **1996**, *49*, 435.

(12) Blades, A. T.; Ikonomou, M. G.; Kebarle, P. *Anal. Chem.* **1991**, *63*, 2109.

(13) Dupont, A.; Gisselbrecht, J. P.; Leize, E ; Wagner, L.; Van Dorsselaer, A. *Tetrahedron Lett.* **1994**, *35,* 6083.

(14) Straub, R. F.; Voyksner, R. D. *J. Am. Soc. Mass Spectrom,* **1993**, *4*, 578.

(15) Coolidge, M. B.; Stewart, J. J. P., Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840, 1990.

(16) Taylor, R. *J. Chem. Soc., Perkin Trans 2* **1993**, 813.