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IONIC PROPERTIES OF HYDROGENATED AND FLUORINATED FULLERENES

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ABSTRACT

The ionization potentials (IP) and electron affinities (EA) for a number of hydrogenated and fluorinated derivatives of C_{60} and C_{70} have been determined using the charge exchange "bracketing" technique. Samples of $C_{60}H_x$ and $C_{70}H_y$ were prepared by direct solid phase hydrogenation ($x=2-18$, $y=2-30$) or platinum oxide catalytic hydrogen reduction ($x=36$, $y=36$). The IP's for $C_{60}H_{2-18}$ are between 6.75 and 7.53 eV for even $x < 10$ and lower than 6.75 for odd $x < 10$. The EAs for $C_{60}F_{44,46,48}$ and $C_{70}F_{52,54}$ were "bracketed" to be 4.0 ± 0.25 eV. The highly fluorinated chiral C_{3h} molecule $C_{60}F_{48}$ was observed to directly attach two electrons in the gas phase to produce $C_{60}F_{48}^{2-}$ and $C_{60}F_{46}^{2-} + F_2$. Studies of the metastable decompositions and collision-induced dissociation of $C_{60}F_{48}^{2-}$ showed fluorine atom and F_2 loss, but no loss of an electron. In addition, the $C_{60}F_{48,46,44}^{2-}$ dianions do not charge exchange with molecules possessing high electron affinities, including the neutral parent compound, $C_{60}F_{48}$ (EA = 4.06 eV). The remarkable stability of $C_{60}F_{48}^{2-}$ to the removal of an excess electron is attributed to a long-range Coulomb barrier which is built from the bound state for the two electrons near the molecule and the electron-electron Coulomb repulsion between the two at large distance.

INTRODUCTION

The most elementary chemical modification (functionalization) of fullerenes consists of hydrogenation and fluorination. Hydrogenated fullerenes show potential as an efficient hydrogen storage medium as well as for fuel cell applications. Fluorinated fullerenes have been suggested as lubricants and are unusual oxidizing and fluorinating agents.[1] Fullerenes are predicted to bind hydrogen atoms inside (endohedral) as well as outside (exohedral) the carbon cage.[2][3][4][5] If fullerenes exist in outer space, they are expected to be hydrogenated and most likely ionized.

The electronic and ionic properties of fullerenes are expected to be dramatically altered upon hydrogenation and fluorination. We report here preliminary studies of the ionic properties (ionization potentials and electron affinities) of a number of hydrogenated and fluorinated derivatives of C_{60} and C_{70} . The measurements are compared to predictions based upon the application of Koopmans' Theorem to published values of the energy levels of the highest occupied (IPs) and lowest unoccupied (EAs) molecular orbitals. In addition, we report on the properties of doubly charged anions of $C_{60}F_{48}$.

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EXPERIMENTAL

Hydrogenation of C_{60} and C_{70} was accomplished in two vastly different methods; 1) direct exposure of fullerenes to high pressure hydrogen gas at elevated temperatures, and 2) catalytic reduction of fullerenes in solution with a platinum oxide catalyst. Direct hydrogenation was achieved by the reaction of C_{60} or C_{70} in the solid phase with high pressure hydrogen gas (500-850 bars) at temperatures ranging from 573 to 623 K. This method resulted in the efficient production of $C_{60}H_x$ for $x=2-18$ and $C_{70}H_y$ for $y=4-30$. Details of this method can be found in a recent paper by Jin, Hettich, Compton, Joyce, Blencoe and Burch.[6]

The second hydrogenation method consisted of solution phase catalytic hydrogen reduction of a mixture of C_{60} and C_{70} (fullerite) using platinum oxide as a catalyst. This method is briefly described below. Catalytic reduction was carried out by preparing a suspension of C_{60}/C_{70} (1.5 mg) and PtO_2 (87 mg) in ethyl acetate (50 mL) in a Parr bottle. The suspension was purged three times with hydrogen gas and placed on a Parr shaker under 35 psi of hydrogen for 7 days at room temperature. The suspension was filtered and the catalyst was washed twice with benzene. The solvent was removed under reduced pressure yielding a viscous yellow oil. TLC analysis (silica gel, 15% benzene in hexanes) indicated two major components ($R_f = 0.55$ and 0.20) which were not UV active (254 nm) but stained with I_2 .

The fluorinated C_{60} was synthesized by reacting C_{60} with fluorine gas. At low or high temperatures, $C_{60}F_{2n}$ ($n \leq 24$) mixtures with various degrees of fluorination were produced.[7] Pure $C_{60}F_{48}$ was generated by using a sodium fluoride matrix in the fluorination reaction at high temperatures.[8] ^{19}F NMR spectroscopy of the sample showed that it consists of an enantiomeric pair have the remaining six double bonds arranged in the chirality-generating orientations.[8]

Mass spectral identification and characterization of these modified fullerenes were performed with either a Fourier transform mass spectrometer (FTMS) [9] or a double focusing magnetic sector/quadrupole hybrid instrument (MSQH).[10] For the FTMS experiments, the modified fullerene samples were placed on the tip of a stainless steel solids probe, which was then inserted into the vacuum chamber of the FTMS. Ions were generated by either laser desorption or thermal desorption of the sample. For laser desorption, the third (355 nm) or fourth harmonic (266 nm) of a Spectra-Physics DCR-11 pulsed Nd:YAG laser was focused onto the sample to provide a laser irradiance of $10^6 - 10^8$ W/cm². A single laser shot was sufficient to desorb and simultaneously ionize the sample. The resulting positive or negative ions could be trapped, studied, and detected in the FTMS cell. For the thermal desorption measurements, the solids probe was controllably heated to temperatures up to 400 °C. These temperatures were sufficient to thermally desorb compounds from the probe, which could then be ionized by electron bombardment (from an electron filament).

In the magnetic sector MSQH instrument, the monoanions and dianions were generated by electron attachment to gas phase $C_{60}F_{48}$ (thermally desorbed from a platinum filament) in the ion source filled with about 1 mTorr of N_2 bath gas. The bath gas is believed to thermalize the electrons and collisionally remove excess vibrational energy of the ions produced upon electron capture. The anions are expelled from the ion source in < 1 μ sec and detected some 90-200 μ s later. Major differences in the two mass spectrometry techniques involve the pressure regime during ionization (10^{-8} Torr in the FTMS and $\sim 10^{-4}$

Torr in the MSQH) and the time scales for ion detection. For the FTMS, ions are trapped for times ranging from 30 ms to several seconds prior to detection, whereas the MSQH mass analyzes ions within a fraction of a millisecond after their formation. As will become apparent, these time scale and pressure differences offer an important distinction which provides complimentary information on the dynamics of the dianion formation and dissociation.

RESULTS AND DISCUSSION

Figure 1 shows the positive ion laser desorption FT mass spectrum of a fullerite sample (C_{60}/C_{70}) after the catalytic hydrogenation reaction. Note that no C_{60}^+ or C_{70}^+ are observed and that the highest level of hydrogenation observed in the mass spectra are $C_{60}H_{36}^+$ and $C_{70}H_{36}^+$. A smaller amount of $C_{60}H_{18}^+$ is also observed. It is difficult to ascertain the exact composition of the sample, because the laser desorption process may induce fragmentation as a result of the ionization process. Thus, it is possible that the sample consists primarily of $C_{60}H_{36}$ and $C_{70}H_{36}$, and the other ions are generated by the laser desorption event. The negative ion laser desorption mass spectrum for this sample did not

Figure 1. Positive ion laser desorption FTMS of fullerene reduction by PtO_2 catalytic hydrogenation (7 days reaction time).

contain any ions corresponding to $C_{60}H_x^-$ or $C_{70}H_y^-$, but revealed minor abundance ions at C_{60}^- and C_{70}^- . Although the positive ion mass spectra indicated that this hydrogenated fullerenes were present in the sample, the absence of negative ions from these species may reflect the small electron affinities of these species. This will be discussed in greater detail in the next section.

In order to investigate whether the PtO_2 catalytic hydrogenation reaction could produce higher hydrogenation levels, this reaction was run for a longer period of time (1 month). The positive ion mass spectra did not contain $C_{60}H_{36}^+$ or $C_{70}H_{36}^+$, but rather revealed ions corresponding to $C_{60}H_x^+$ for $x < 20$. The negative ion mass spectra, shown in Figure 2, indicated $C_{60,70}H_x^-$ for $x=0-10$ and the presence of fullerene hydroxides (the ion at m/z 801 does not have the ^{13}C isotopic abundances consistent with fullerenes, and thus was not examined in detail). Although we have not studied this reaction extensively, it appears that the longer reaction time did not extend the hydrogenation level. It is interesting to note that the extended hydrogenation of C_{60} with dihydroanthracene [11] does not generate hydrogenation above $C_{60}H_{36}$, but rather produces $C_{60}H_{18}$, indicating that $C_{60}H_{36}$ is a good hydrogen donor to anthracene (which is a by-product in the reaction).

Figure 2. Negative ion laser desorption FTMS of fullerene reduction by PtO_2 catalytic hydrogenation (1 month reaction time).

Fullerene hydrogenation was also examined using a lithium/ethylenediamine (Li/EDA) reduction reaction, which is useful for reducing aromatic hydrocarbons to alkanes (benzene can be reduced to cyclohexane). [12] These reactions conditions are sufficient to reduce

isolated double bonds and should provide more extensive hydrogenation conditions than the Birch reduction (Li/NH_3). Reducing C_{60} with Li/EDA (2-4 hours reaction time) generated $\text{C}_{60}\text{H}_{36}$ as the highest hydrogenation product, as determined by mass spectrometry. Examination of longer reaction times did not reveal a higher hydrogenation level; in fact, the use of long reaction times (> 7 hours) was found to degrade the hydrogenated fullerene to lower levels (C_{60}H_x , $x < 36$).

For the direct hydrogenation method, solid phase C_{60} contained in a AgPd capsule was exposed to a 975 bars hydrogen/argon atmosphere (650 bars partial pressure of H_2) at 573 K for 119 hours. The positive ion laser desorption mass spectrum of the resulting sample revealed the presence of $\text{C}_{60}\text{H}_x^+$ for $x = 2-18$. [6] Although a higher degree of hydrogenation may have been present in this sample, $\text{C}_{60}\text{H}_{18}^+$ is the highest member clearly evident in the mass spectrum. Because we have previously detected both $\text{C}_{60}\text{H}_{18}^+$ and $\text{C}_{60}\text{H}_{36}^+$ as products of the platinum oxide catalytic hydrogenation of C_{60} in solution with these same mass spectrometry experimental conditions, it seems likely that $\text{C}_{60}\text{H}_{18}$ reflects the highest degree of hydrogenation generated at these temperatures and pressures. The most abundant positive ions in the mass spectra were centered around C_{60}H_x with $x = 10-15$. A clear odd/even (number of hydrogens) alternation is observed in the mass spectrum with odd numbered peaks more abundant than their even numbered neighbors. We ascribe this alternation to the ionization process and not the neutral distribution. Based on stability considerations, the actual species in the sample were probably all even hydrogen-containing fullerene species; however, dissociative ionization would generate the more energetically stable odd-numbered ions. Although argon was used in the gas mixture, $\text{Ar}@\text{C}_{60}$ ions were not observed in the mass spectra.

The negative ion mass spectrum contained $\text{C}_{60}\text{H}_x^-$ ions for $x=0-10$, suggesting a lower degree of hydrogenation than the positive ion spectrum; however, this spectrum probably reflects the greater stability of the lower hydride negative ions. Dissociative electron attachment (i.e., $e + \text{C}_{60}\text{H}_{18} \rightarrow \text{C}_{60}\text{H}_{18-x}^- + \text{H}_x$ for $x = 1-18$) is expected to preferentially generate the most abundant ions to be those with the largest electron affinities. Thus, the degree of fullerene hydrogenation is difficult to ascertain from the negative ion mass spectra because of the differences in ionization efficiencies and the possibility of dissociative ionization processes to preferentially generate the most stable negative ions. Of course, non-dissociative electron attachment is expected to occur as well.

This C_{60}H_x sample could be stored as a solid at ambient conditions for at least two months with no measurable degradation, as verified by repeated mass spectral examination. This observation is in marked contrast to the Birch reaction [13] and catalytic hydrogenation samples, which showed substantial dehydrogenation after a relatively short time, and the interstitial H_2 fullerene sample of Assink and coworkers [14], which had a half-life of only 30 minutes.

IP Determinations for C_{60}H_x

It is possible to determine upper and lower limits to the ionization potentials of the hydrogenated fullerenes by using the charge exchange "bracketing" reaction shown below:

If reaction 1 is observed, then the ionization potential of C_{60}H_x must be higher than that of reagent A. Experimentally, this would correspond to a decrease in abundance of $\text{C}_{60}\text{H}_x^+$ with increasing reaction time and an increase in the abundance of A^+ . Both ions need to be monitored in order to verify that this is the only reaction occurring, and that proton transfer or some other reaction does not complicate the spectra. The absence of any products for reaction 1 would imply that the I.P. of A is higher than the I.P. of the hydrogenated fullerenes, although this must be viewed with caution because other factors may be involved in the absence of reactions. In order to check our charge exchange experiments for a known reaction, C_{60}^+ was reacted with gas phase azulene. Charge transfer was observed under these conditions, as evidenced by a decrease in the abundance of C_{60}^+ and an increase in m/z 128 ($\text{C}_{10}\text{H}_8^+$, the molecular ion for azulene). This result verifies that the ionization potential of azulene (I.P. = 7.41 eV [15]) is lower than the value for C_{60} (I.P. = 7.6 eV [16]), and indicates that our charge exchange experiments should be useful for determining the direction of electron transfer even for species with small differences in ionization potentials.

The C_{60}H_x ($x=2-18$) sample generated by the high pressure hydrogenation process was used for examination of charge transfer reactions listed below. No reaction was observed between $\text{C}_{60}\text{H}_x^+$ and 1-methylnaphthalene (I.P. = 7.85 eV [15]) or 1,4-dimethoxybenzene (I.P. = 7.53 eV [15]). This implies that the I.P.s of the hydrogenated fullerenes are lower than 7.53 eV. Thus, hydrogenation at this level ($x < 18$) lowers the ionization potentials of the hydrogenation species relative to the parent C_{60} .

Charge exchange (reaction 1) was observed for A = ferrocene (I.P. = 6.75 eV [15]) for $\text{C}_{60}\text{H}_x^+$ where $n = 2-4,6,8,10$, and 12, but did not occur for $x = 5,7,9,11,13-15$. Experimentally, the abundances of the $\text{C}_{60}\text{H}_x^+$ ions for $x = 0-4,6,8,10,12$ decrease with reaction time, while the abundances of the other $\text{C}_{60}\text{H}_x^+$ ions are virtually unchanged. The ionic product of the charge exchange reaction, which is the molecular ion of ferrocene (m/z 186), increases with reaction time.

The charge exchange results outlined above provide the upper and lower bounds necessary to bracket the ionization potentials of C_{60}H_x for $x = 2-4,6,8,10,12$ to values between 7.53 (the I.P. of 1,4-dimethoxybenzene) and 6.75 eV (the I.P. of ferrocene). The I.P.s for C_{60}H_x for odd-numbered $x > 3$ are lower than 6.75 eV. The I.P.s for C_{60}H_x for $x = 14,16,18$ appear to be lower than 6.75 eV, although this result must be viewed with caution because the ion abundances in this region are quite low and it is difficult to differentiate the isobaric $^{12}\text{C}_{60}\text{H}_x^+$ ($x=\text{even}$) from the more abundant $^{13}\text{C}_1^{12}\text{C}_{59}\text{H}_x^+$ ($x=\text{odd}$). Although this range is quite wide, it is interesting to note that the I.P.s of the hydrogenated C_{60} are lower than the value for C_{60} itself (I.P. = 7.6 eV).

To our knowledge, there are no published experimental ionization potentials for hydrogenated fullerenes. However, estimates of the I.P.'s can be obtained by applying Koopmans' theorem to theoretical calculations of the energy level of the highest occupied molecular orbital (HOMO). We have plotted in Figure 3 the predicted I.P. for $\text{C}_{60}\text{H}_{2n}$ by using such an analysis based on calculated HOMO orbital levels.[17] We have empirically fixed the I.P. of C_{60} to the known experimental value of 7.6 eV in order to obtain more reliable estimates of the values for $\text{C}_{60}\text{H}_{2n}$ (only values for 1,2 hydrogen addition are shown). The calculated I.P.s for C_{60}H_x from Matsuzawa et.al. (used here because values are available for the lower numbers of hydrogens) appear to decrease relatively uniformly from

$x = 0$ to 20, reach a minimum in the range of $x = 20$ -38, and then increase for $x > 38$. The experimental data outlined above support the first section of this theoretical plot, in particular verifying that the I.P.s of $C_{60}H_x$ for $x < 10$ are below that of C_{60} and are between 6.75 and 7.53 eV, whereas the I.P.s for $x > 12$ appear to be lower than 6.75 eV. Because of the hydrogenation level of this sample, it was not possible to examine the experimental IPs for highly hydrogenated C_{60} . These experiments will be examined in future work.

Figure 3. Estimated ionization potentials for $C_{60}H_x$ obtained by applying Koopmans' theorem to the energy levels of the HOMO from ref. 17.

Although limited experimental studies were carried out for the negative ions of $C_{60}H_x$, the electron affinities for this series can also be estimated by application of Koopmans' theorem to the calculated lowest unoccupied molecular orbitals, or LUMOs of Matsuzawa et.al. [17]. Once again, the calculations for $C_{60}H_x$ are referenced to the experimentally-determined electron affinity of C_{60} (2.7 eV). The calculated electron affinities for $C_{60}H_x$ are observed to decrease rapidly with increasing x and seem to approach zero at $x = 20$ -30. It would seem reasonable to ascribe the precipitous decrease of our measured $C_{60}H_x^-$ intensities with increasing x to a similar decrease in electron affinities. Furthermore, stable negative ions are not expected for $x > 20$. Experimentally, we have been unable to observe negative ions of $C_{60}H_x$ for $x > 10$ in other hydrogenated samples. For example, in samples where $C_{60}H_{36}^+$ was observed in high abundance, the corresponding negative ions were not present.

EA Determinations for $C_{60}F_x$

Reactions 2 and 3 illustrate the processes that were examined to bracket the electron affinity of the fluorinated fullerenes.[18] Reaction 2 involves gas phase reaction of

reagent ion A^- with the neutral $C_{60}F_x$. Experimentally, this is accomplished by isolating a given reagent ion, such as NO_2^- , and then trapping that ion in the presence of neutral $C_{60}F_x$ generated by thermal desorption of the sample from the solids probe. If $C_{60}F_x^-$ is observed as a product of reaction 2, then the electron affinity of the fluorinated fullerene must be larger than the electron affinity of reagent A . Reaction 3 is essentially the reverse of reaction 2 and is accomplished by reacting $C_{60}F_x^-$ with the neutral A . Examination of both reactions 2 and 3 provides redundant information; however, this is often necessary to ascertain unambiguously the direction of electron transfer. In some cases, especially with the higher electron affinity reagents, it was not possible to monitor reaction 3 since the appropriate neutral could not be obtained (atomic Cl for example). By examining reactions 2 and 3 for reagents with different electron affinities, it was possible to "bracket" (i.e. determine upper and lower bounds) the electron affinities of the fluorinated fullerenes.

Reactions 2 and 3 were examined for a variety of reagents with electron affinities ranging from 2.21 eV (phenoxide) to 4.46 eV (ReO_4^-).^[15] $C_{60}F_x$ ($x=44,46$) will undergo electron transfer with all negative ions of reagents which have electron affinities below that of NO_3^- (EA = 3.92 eV [15]), but will not charge exchange with the negative ions of CF_3COO^- (EA = 4.20 eV [15]) and ReO_4^- (EA=4.46 eV [15]). Similar reaction results were obtained for $C_{70}F_y$ ($y=52,54$). These experiments provided the following bracketed electron affinity values:

$$EA(C_{60}F_{44,46}) = 4.06 \pm 0.25 \text{ eV}$$

$$EA(C_{70}F_{52,54}) = 4.06 \pm 0.25 \text{ eV}$$

The error bars are estimated based on the combined uncertainties and range of values of the electron affinities of the bracketing reagents. Further experiments clearly established that $EA(C_{70}F_{54,52}) > EA(C_{60}F_{46,44})$, which is reminiscent of the fact that $EA(C_{70}) > EA(C_{60})$. The higher EA may also be related to the higher number of fluorines attached to the C_{70} as well.

The electron affinities of $C_{60}F_x$ were found to be almost 1.5 eV higher than that of C_{60} (EA = 2.65 eV [19]). These results imply that fluorination has substantially altered the electronic energy levels of the corresponding pure fullerenes. Together with the indication that $C_{60}F_x$ ($x=44,46$) have higher ionization potentials than C_{60} , these results would suggest that the HOMO and LUMO levels are shifted downward considerably in energy by fluorination, perhaps due to the electronegativity of fluorine. Thus, even though fluorination

of fullerenes reduces many of the double bonds in the fullerene and destroys conjugation, the addition of electronegative fluorine atoms compensates for this loss and in fact increases the electron affinity. For comparison, preliminary theoretical results of G. Scuseria for $C_{60}F_{48}$ (t_h symmetry) obtained using dzvd/SCF calculations at MNDO optimized geometries have yielded a calculated electron affinity of approximately 5 eV. [20]

Doubly-Charged Anions of $C_{60}F_x$

We have observed the unexpected direct attachment of two electrons to the fluorinated fullerene molecule $C_{60}F_{48}$ in the gas phase.[21] Both non-dissociative and dissociative electron attachment to a negative ion are observed.

Two different mass spectrometry techniques, FTMS and magnetic sector/quadrupole instrument, were employed to identify and characterize the doubly-charged anions for the fluorinated fullerenes. For the FTMS experiments, the fluorinated fullerene solids were thermally desorbed (250-300 °C) from a stainless steel probe in the vacuum chamber of the FTMS, and were then ionized by the attachment of low energy electrons from an electron beam. Two different $C_{60}F_x$ samples were examined. The first sample, which is predominantly $C_{60}F_{46}$, showed $C_{60}F_{46}^-$ as the most abundant ion and some $C_{60}F_{44}^-$ in the mass spectrum, along with a small amount of the dianions, primarily $C_{60}F_{44}^{2-}$ (presumably formed by dissociative electron capture). Ion ejection techniques and inspection of the spacing and abundances of the isotopic peaks, which were useful for identifying dianions of C_{60} and C_{70} [22] [23], provided further evidence that the $C_{60}F_{42}^{2-}$, $C_{60}F_{42}O^{2-}$, $C_{60}F_{44}^{2-}$, $C_{60}F_{44}O^{2-}$, $C_{60}F_{46}^{2-}$, and $C_{60}F_{46}O^{2-}$ were true dianions trapped in the FTMS cell and not second harmonics of the monoanions or other contaminants from the sample. Examination of the second sample, a single isomer of $C_{60}F_{48}$ (containing some $C_{60}F_{46}O$), revealed primarily monoanions at $C_{60}F_{48}^-$ and dianions of $C_{60}F_{46}^{2-}$ (with a smaller amount of $C_{60}F_{48}^{2-}$).

In the magnetic sector MSQH instrument, the monoanions and dianions were generated by electron attachment to gas phase $C_{60}F_{48}$ (thermally desorbed from a platinum filament) in the ion source filled with about 1 mTorr of N_2 bath gas. The bath gas is believed to thermalize the electrons and collisionally remove excess vibrational energy of the ions produced upon electron capture. The anions are expelled from the ion source in < 1 μ sec and detected some 90-200 μ s later. Both monoanions and dianions were observed in the negative ion mass spectra. $C_{60}F_{48}^-$ was the most abundant singly charged anion. In contrast to the dianion mass spectrum from the FTMS, $C_{60}F_{48}^{2-}$ was found to be the most abundant dianion in the magnetic sector apparatus. The $C_{60}F_{48}^{2-}$ dianion was found to be metastable with respect to F_2 , F, and F^- losses. Within the time window of 90 to 145 microseconds, some of the $C_{60}F_{48}^{2-}$ ions dissociate to $C_{60}F_{46}^{2-}$ (F_2 loss), $C_{60}F_{47}^{2-}$ (F loss), and $C_{60}F_{47}^-$ (F^- loss). Upon medium energy collisions (200 eV) with argon gas, $C_{60}F_{48}^{2-}$ displayed fragments of $C_{60}F_{44}^{2-}$ ($2F_2$ loss), $C_{60}F_{45}^-$ ($F_2 + F^-$ loss), and $C_{60}F_{43}^-$ ($2F_2 + F^-$ loss). *The most significant result from both of these experiments is that electron detachment from $C_{60}F_{48}^{2-}$ is not observed in either the metastable decay or collisional dissociation spectra.* For comparison, the low energy collision-induced dissociation (50 eV collision energy) of C_{70}^{2-} reveals only electron detachment as the fragmentation pathway. [24]

The charge exchange reaction 4 was examined in an attempt to bracket the second electron affinities:

Specifically, trapping $\text{C}_{60}\text{F}_{44}^{2-}$ in the presence of gas phase tetrafluoro-1,4-benzoquinone (fluoranil, EA = 2.7 eV [15]) or 7,7,8,8-tetracyanoquino-dimethane (TCNQ, EA = 3.3 eV [18]) for up to 30 sec, produced no reaction. Also, the doubly charged $\text{C}_{60}\text{F}_{44}^{2-}$ ions could be trapped for the same amount of time in the presence of gas phase C_{60}F_x neutrals (EA = 4.06 eV [18]) with no appreciable loss of dianion signal or appearance of singly-charged $\text{C}_{60}\text{F}_x^{-}$ ions. Because the electron affinities of these reagents are almost certainly larger than the electron affinity of $\text{C}_{60}\text{F}_{44}^{-}$, the absence of charge exchange provides evidence for a large exit barrier for electron abstraction from the dianion. This is reasonable, since the Coulomb barrier to attachment of the second electron to the monoanion $\text{C}_{60}\text{F}_x^{-}$ should also affect the removal of the second electron from the dianion. The absence of charge exchange reactions suggests that the electron affinity plus the exit barrier for electron abstraction from $\text{C}_{60}\text{F}_{44}^{2-}$ is equal to or greater than ~ 4.06 eV (the EA of $\text{C}_{60}\text{F}_{44-48}$).

Additional stability occurs as a result of the Coulomb barrier to the removal of either excess electron. To investigate this effect, the interaction potential for an electron with a singly-charged sphere of radius a and dielectric constant k was calculated. We estimate the polarizability of $\text{C}_{60}\text{F}_{48}$ to be $84 \text{ \AA}^3$, as compared to $80 \text{ \AA}^3$ for C_{60} , and thus take k to be the same as that of C_{60} (4.4). [25] The radius of the sphere is taken as that of C_{60} plus a C-F bond length ($\sim 5 \text{ \AA}$). The ($\ell = 0$) Coulomb barrier is found to be on the order of 1.5 eV and the total energy required to remove either excess electron must exceed this barrier plus the second electron affinity. This simple but realistic model provides a rationalization for the exceptional stability of $\text{C}_{60}\text{F}_{48}^{2-}$ with respect to electron detachment as a result of collisions or reactions. This result is expected to be generally applicable to molecular dianions.

CONCLUSIONS

This study represents an initial step in the experimental study of the ionic properties of hydrogenated and fluorinated fullerenes. The preliminary experimental results of the ionization potentials for $\text{C}_{60}\text{H}_{2n}$ are in general agreement with theoretical predictions employing Koopmans' theorem. Also, a new method of catalytic hydrogen reduction of C_{60} and C_{70} is described. The first electron affinity of $\text{C}_{60}\text{F}_{48}$ was determined to be large (4.06 eV). Mass spectrometry studies have indicated that $\text{C}_{60}\text{F}_{48}^{2-}$ can be generated by the attachment of two electrons in the gas phase. The dianion shows extreme stability with respect to electron loss, which is attributed to a Coulomb barrier to electron removal.

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