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Thermochemistry of the Gas Phase Reactions of Fluorofullerene Anions

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The ion−molecule equilibrium method has been applied to studies of the gas phase fluorine exchange reactions between fullerene anions and metal fluoride anions. This has yielded the first quantitative determination of the absolute values of Gibbs energies for addition of fluorine to the anions of higher fullerenes C_{70+2n}^- (n = 0, 1, ..., 7) and sequential fluorine addition in the series $C_{60}F_n^-$ (n = 0, 1, 2). Estimates for C−F bond dissociation energies of $C_{60}F_2$ and $C_{70}F_2$ and electron affinities of monofluorinated [60]- and [70]fullerenes in the gas phase are reported.

Introduction

Both gas phase chemistry and thermochemistry are of fundamental importance in many fields of fullerene science. Studies on gas phase ion−molecule reactions involving singly and multiply charged fullerene species provide better insight into the chemical reactivity and stability of fullerenes and derivatives. In some cases gas phase reactivity trends can be extrapolated to reactions in solution. For example, for the higher fullerene series and some endohedral metallofullerenes, a remarkably linear correlation was found between the reduction potentials in solution and electron affinities in the gas phase.[1]

Theoretical calculations have indicated that molecular anions are less reactive than the corresponding cations.[2] Few studies have been published on the gas phase chemistry of fullerene anions in contrast to the reactions of the cations of fullerenes.[3] At room temperature C_{60}^- reacted with NO_2, and an intense $C_{60}NO_2^-$ peak was registered in the mass spectrum.[4] Interaction of C_{60}^- with O_2 in the gas phase yielded $C_{60}O_n^-$ (n = 1, ..., 4).[5] Observation of $C_{60}F_n^-$ (n = 1, 2) by the chemical ionization (CI) mass spectrometry method has been reported.[6]

Several studies on the energetics of electron transfer reactions involving anions of fullerenes and their derivatives in the gas phase have been made.[7−13]

We reported recently the method of generation of difluorinated fullerene molecules and anions at elevated temperatures and determination of the EA's of difluorinated [60]- and [70]fullerenes which gave slightly higher values (~0.2 eV) than those for the parent fullerenes.[13]

Here we describe the first quantitative thermochemical data on the absolute values of Gibbs energies for fluorine addition to the higher fullerene anions C_{70+2n}^- (n = 0, 1, ..., 7) and sequential fluorine addition in the series $C_{60}F_n^-$ (n = 0, 1, 2). We also report our estimate of C−F bond dissociation energies for difluorinated [60]- and [70]fullerenes and electron affinities of monofluorinated [60]- and [70]fullerenes in the gas phase.

Experimental Section

The experimental method employed is the ion−molecule equilibrium method (IME) which is a modified version of the Knudsen cell mass spectrometry method. A diagram of the experimental setup is shown in Figure 1.

The operation of the instrument and the experimental conditions are briefly described. The positive ion mode of the combined ion source is a conventional electron ionization technique which permits determination of the neutral vapor composition and partial pressure. Cations are formed in the ionization chamber via electron bombardment (70 eV) of molecules evaporating from the effusion cell.

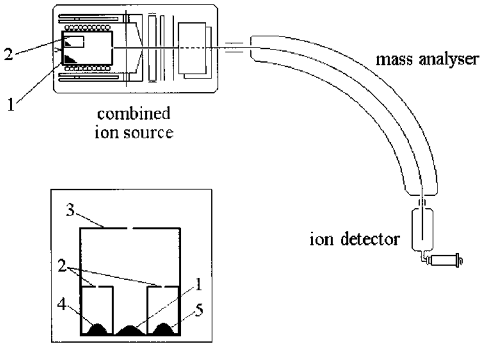

Figure 1. Scheme of the experimental setup for the IME studies: (1) alkali metal salt (KF−HF); (2) platinum ampoules; (3) effusion cell; (4) $C_{60}F_{46}$; (5) fullerene sample.

A thermal negative ion mode is also available in the instrument. The effusion cell is at high (−2 kV) potential; the electron beam is switched off. Extraction of anions by a weak electrostatic field is followed by the monitoring of negative ion mass spectra. The anions are generated inside the effusion cell as a result of surface thermal ionization, and they are in equilibrium with the neutral species at the given temperature. Verification of the equilibrium is based on the mass action law, and it was previously performed on the higher fullerene systems.[8,12]

The experiment is carried out under the effusion conditions when the mean free path of the species in the gas phase far exceeds the linear sizes of the cell and collisions in the gas phase are practically negligible. Therefore equilibrium in the system is established through the collisions with the walls of the cell. Similarly, products of the chemical reactions observed in the present study are formed as a result of interactions in the solid phase or on the surface but not through the direct collisions of the gas phase species.

Thus sequential measurements of the mass spectra of positive and negative ions provide data on partial pressures of both neutral and charged (negative) species, and equilibrium constants of ion−molecule, molecule−molecule, and ion−ion reactions in the gas phase can be studied. The procedures involved have been described previously.[14]

In the present work the fluorine exchange ion−ion reactions were studied:

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$$C_mF_2^- + C_n^- = C_m^- + C_nF_2^-$$

$$K_p = P_{C_nF_2^-}P_{C_m^-}/P_{C_n^-}P_{C_mF_2^-} \qquad (1)$$

Using eq 1 and the relationship between partial pressure and the ion intensity of an anion j, one can obtain an equilibrium constant value from the measured ion intensities (I_j) of anions and their molar masses (M_j):

$$K_p = I_{C_nF_2^-}I_{C_m^-}[M_{C_nF_2^-}]^{1/2}[M_{C_m^-}]^{1/2}/ I_{C_n^-}I_{C_mF_2^-}[M_{C_n^-}]^{1/2}[M_{C_mF_2^-}]^{1/2} \qquad (2)$$

The temperature of the effusion cell was measured by a Pt−Pt/Rh thermocouple. Nickel and platinum effusion cells with the inner surface to effusion area ratio of ca. 500 were used. Fullerenes were loaded into a separate Pt container with a hole smaller than the orifice in the effusion chamber in order to reduce the partial pressure of fullerenes and by this means to extend the experimental temperature range. Thus reduction of the partial pressure of fullerenes by a factor of 50−100 could be achieved. Then (see Figure 1), an ampoule with fullerenes was placed into the effusion cell together with inorganic fluorides and small amounts of alkali metal oxo- or fluorosalt. The latter was used to reduce the work function of the inner surface of the cell, thereby enabling effective negative ion generation at elevated temperatures. When fluorinated fullerene was used, a fluorinating agent was placed into the second container—separately from the fullerene mixture (inset in Figure 1).

The experimental conditions (compositions of the systems, temperatures) and the anions of fluorofullerenes identified in the negative ion mass spectra are presented in Table 1. Fluorofullerenes were formed as a result of the reaction of fullerenes and metal fluorides (systems 1, 2, and 4) or highly fluorinated fullerenes (system 3), and the corresponding anions were observed in the mass spectra along with the anions of parent fullerenes and metal fluoride anions.

Results and Discussion

Gibbs Energies of Fluorine Addition Reactions. Gibbs energy change values of the observed reactions were calculated using eq 3:

$$\Delta G^0_T = -RT \ln K_p \qquad (3)$$

The averaged Gibbs energies for reactions 1−15 are summarized in Table 2.

By combining reactions 1 and 2, one obtains reaction 19:

$$FeF_4^- + UF_5^- = FeF_3^- + UF_6^- \qquad (19)$$

The value of $\Delta G^0_T(19) = 12.6$ kJ/mol derived from our experiment is consistent with the previously published data ($\Delta G^0_{1083}(19) = 11.3$ kJ/mol).[15]

Reactions 1−14 represent combinations of two semireactions of fluorine addition. Therefore the obtained Gibbs energy data directly provide the relative energies of fluorine addition in the fullerene series. To derive the absolute Gibbs energy values of reaction 20

$$C_n^- + xF = C_nF_x^- \qquad (20)$$

one needs to know $\Delta G^0_T(20)$ for at least one of the ions involved in reactions 1−14.

TABLE 1: Gas Phase Fluorofullerene Anions Observed in the "Fullerene-Fluorinating Agent" Systems

no. of system	fluorinating agent	T, K	$C_nF_m^-$
1	$FeF_3 + UF_4$ (50:50)	957−1071	$C_{60}F^-$
2	FeF_3	920−976	$C_{60}F_2^-$, $C_{60}F_4^-$
3	$C_{60}F_{46}$	957−1072	$C_{60}F^-$, $C_{60}F_2^-$, $C_{60}F_4^-$ $C_{70+2k}F_2^-$ (k = 0, 1, ..., 7)
4	CuF_2	826−951	$C_{60}F^-$, $C_{70}F^-$

TABLE 2: The Experimental Results of Gibbs Energy Change of Ion−Ion Reactions

reaction	system		no. of runs	ΔG^0_T, kJ/mol
1	1	$C_{60}^- + FeF_4^- = C_{60}F^- + FeF_3^-$	22	47.1 ± 1.7
2	1	$C_{60}^- + UF_6^- = C_{60}F^- + UF_5^-$	22	34.5 ± 3.1
3	2	$C_{60}^- + 2FeF_4^- = C_{60}F_2^- + 2FeF_3^-$	4	136.3 ± 6.0
4	2	$2C_{60}F^- = C_{60}F_2^- + C_{60}^-$	2	22.0 ± 0.2
5	2	$C_{60}F_4^- + C_{60}^- = 2C_{60}F_2^-$	2	−79.2 ± 1.5
6	3	$C_{60}F_2^- + C_{70}^- = C_{60}^- + C_{70}F_2^-$	4	4.7 ± 2.6
7	3	$C_{60}F_2^- + C_{72}^- = C_{60}^- + C_{72}F_2^-$	1	−30.4 ± 4.5
8	3	$C_{60}F_2^- + C_{74}^- = C_{60}^- + C_{74}F_2^-$	1	−52.0 ± 4.5
9	3	$C_{60}F_2^- + C_{76}^- = C_{60}^- + C_{76}F_2^-$	1	−23.2 ± 4.5
10	3	$C_{60}F_2^- + C_{78}^- = C_{60}^- + C_{78}F_2^-$	1	−25.8 ± 4.5
11	3	$C_{60}F_2^- + C_{80}^- = C_{60}^- + C_{80}F_2^-$	1	−49.4 ± 4.5
12	3	$C_{60}F_2^- + C_{82}^- = C_{60}^- + C_{82}F_2^-$	1	−44.6 ± 4.5
13	3	$C_{60}F_2^- + C_{84}^- = C_{60}^- + C_{84}F_2^-$	2	−38.6 ± 4.5
14	4	$C_{60}^- + C_{70}F^- = C_{60}F^- + C_{70}^-$	8	6.70 ± 2.5
15	4	$C_{60} + C_{70}^- = C_{60}^- + C_{70}$	9	8.89 ± 2.0
16	4	$C_{60} + C_{60}F^- = C_{60}F + C_{60}^-$		≥25.2
17	4	$C_{70} + C_{60}F^- = C_{60}F + C_{70}^-$		≥15.4
18	4	$C_{60} + C_{70}F^- = C_{70}F + C_{60}^-$		≥30.3

TABLE 3: Gibbs Energies and Enthalpies of the Reactions of Fluorination of Fullerene Anions

no. of reaction		ΔG^0_T, kJ/mol[a]	ΔH^0_0, kJ/mol	BDE, kJ/mol
20.1	$C_{60}^- + 2F = C_{60}F_2^-$	−496	−744	372
20.2	$C_{70}^- + 2F = C_{70}F_2^-$	−492	−740	370
20.3	$C_{72}^- + 2F = C_{72}F_2^-$	−527	−774	387
20.4	$C_{74}^- + 2F = C_{74}F_2^-$	−548	−796	398
20.5	$C_{76}^- + 2F = C_{76}F_2^-$	−519	−767	384
20.6	$C_{78}^- + 2F = C_{78}F_2^-$	−523	−770	385
20.7	$C_{80}^- + 2F = C_{80}F_2^-$	−546	−793	397
20.8	$C_{82}^- + 2F = C_{82}F_2^-$	−541	−788	394
20.9	$C_{84}^- + 2F = C_{84}F_2^-$	−535	−782	391
20.10	$C_{60}^- + F = C_{60}F^-$	−267	−388	388
20.11	$C_{70}^- + F = C_{70}F^-$	−274	−395	395
20.12	$C_{60}F^- + F = C_{60}F_2^-$	−237	−361	361
20.13	$C_{60}F_2^- + 2F = C_{60}F_4^-$	−412	−665	332
20.14	$C_{60} + F = C_{60}F$	≥−242	≥−363	≤363
20.15	$C_{70} + F = C_{70}F$	≥−253	≥−374	≤374

[a] Each value ±20 kJ/mol.

Hitherto, no experimental data on the energetics of fluorine addition have been obtained for fluorofullerene anions. Hence, as anchor compounds we used metal fluorides in systems 1 and 2. FeF_3 and UF_4 were studied previously by the IME method, and thermodynamic functions of the reactions of fluorine addition to the neutral and negatively charged metal fluorides were measured accurately.[15]

Thus using data on Gibbs energies of reactions 21 and 22[15]

$$FeF_3^- + F = FeF_4^- \qquad (21)$$

$$UF_5^- + F = UF_6^- \qquad (22)$$

we calculated absolute values of Gibbs energies of reactions of fluorine addition to fullerene anions (Table 3).

Partial Pressure of Fluorine. The use of transition metal fluorides in the IME experiments allows one to monitor the fluorine pressure in the system and thereby to control the fluorination products. It was found in the late 1980s that, due to the formation of negatively charged species in different oxidation states in the high-temperature vapors of transition metal fluorides, the partial fluorine pressure could be determined in the system of interest.[16] A number of transition metal fluoride systems were studied, and thermodynamic functions for reactions

$$MF_n^- + F = MF_{n+1}^- \qquad (23)$$

were determined. Thus, by measuring the $I_{M_{Fn+1-}}/I_{M_{Fn-}}$ ratio experimentally and using the known value of the equilibrium constant $k_p(23)$ one can obtain the partial pressure of fluorine in the system, provided all the components of the system are under thermodynamic equilibrium conditions:

$$P_F = (I_{M_{F_{n+1^-}}}/I_{M_{F_{n^-}}})(1/k_p(23)) \qquad (4)$$

Anions FeF_3^- and FeF_4^- as well as UF_5^- and UF_6^- were found in the mass spectra of systems 1 and 2 along with the fluorofullerene peaks, and corresponding reactions of exchange of fluorine with the fullerene anions were studied (Table 2). Variation of the FeF_3^-/FeF_4^- ratio in systems 1 and 2 (0.003 and 100, respectively, at 950 ± 5 K) is indicative of the change of the partial pressure of fluorine; therefore, the presence of di- and tetrafluorinated fullerene species in system 2 can be accounted for by the higher pressure of fluorine whereas in system 1 only monofluorofullerene anions were observed.

Bond Dissociation Energy of Fluorofullerene Anions. One can reasonably assume the entropy of isomolecular gas phase reactions 1−18 to be close to zero. It follows from eq 5

$$\Delta H^0_0 = \Delta\Phi^0_T T + \Delta G^0_T \qquad (5)$$

that if $\Delta\Phi^0_T \cong 0$,

$$\Delta H^0_0 \cong \Delta G^0_T \qquad (6)$$

Using the above assumption and the experimental data on Gibbs energies of reactions 1−14 (Table 2) together with the literature data on the enthalpies of reactions 21 and 22, we calculated enthalpies of reactions 20.1−20.15 involving fullerene anions C_{60+2n}^- (n = 5, 6, ..., 12). The results given in Table 3 also include the calculated C−F bond dissociation energies (BDE) per bond.

Interestingly, plots of the reversed enthalpies of reactions 20.1−20.9 which characterize affinity of fullerene anions to fluorine (FA) and electron affinities of higher fullerene molecules[12] as a function of the number of carbon atoms (Figure 2) uncovered similar trends of both thermodynamic quantities in the fullerene series. Furthermore abnormally high values of FA should be noted for n(C) = 74 as it was previously found for EA(C_{74})[12] while [60]- and [70]fullerenes have the lowest in the series and practically the same values of FA and EA. The detailed analysis of electronic structure of fullerene molecules and their anions must be called on to explain the observed regularities in FA and EA change in the higher fullerene series.

Strictly speaking, the obtained thermodynamic quantities should be related to the mixture of isomers of the higher fullerenes. It is well-known that in the raw fullerene soot higher fullerenes ($C_{n>74}$) are present as mixtures of two (C_{84}) or even more isomers—the number of isomers increases dramatically with the size of the molecule. Although some progress has been achieved in separating single isomers of higher fullerenes,[17] they are still not readily available in milligram quantities which are required to perform mass spectrometry studies. Therefore at this stage it is not possible to obtain experimentally thermodynamic data on the reactions involving single isomers of the higher fullerenes. To our knowledge no theoretical calculations have been published on the relative energies of the fluorine addition to the various isomers of the higher fullerenes.

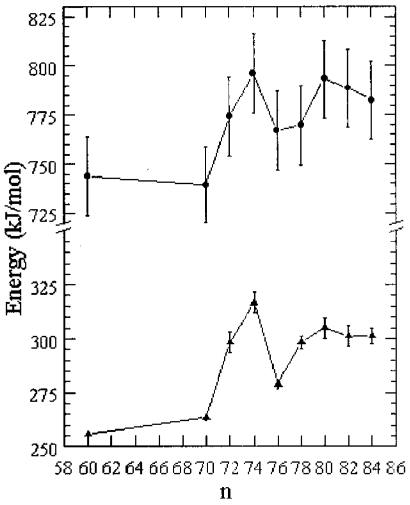

Figure 2. Plot of the fluorine affinity (FA) of fullerene anions (solid circles) and the electron affinity (EA) of fullerenes[12] (solid triangles) as a function of the number of carbon atoms. The verticle lines show total uncertainties in FA and EA values.

$$\begin{tikzcd}
C_n + 2F \arrow[r, "\Delta H(1)"] \arrow[d, "+e"', "EA(C_n)"] & C_nF_2 \arrow[d, "+e"', "EA(C_nF_2)"] \\
C_n^- + 2F \arrow[r, "\Delta H(2)"] & C_nF_2^-
\end{tikzcd}$$

Figure 3. Thermodynamic cycle for the calculation of BDE($C_{60}F_2$) and BDE($C_{70}F_2$).

TABLE 4: BDE of $C_{60}F_2$ and $C_{70}F_2$ and Electron Affinities of $C_{60}F$ and $C_{70}F$

	60	70	ref
EA(C_n), kJ/mol	256	−	7
	257[a]	258	9
		265[a]	12
EA(C_nF_2), kJ/mol	263	272	13
ΔH^0_0 (2), kJ/mol [b]	−743	−739	this work
ΔH^0_0 (1), kJ/mol[b]	−736	−732	this work
BDE (C_nF_2), kJ/mol	369	366	this work
	365		17
EA(C_nF), kJ/mol	≥283	≥288	this work
	≥268		13

[a] Values used for calculations. [b] For reaction, see Figure 3.

Bond Dissociation Energy of Difluorinated [60]- and [70]Fullerenes. Using the thermochemical cycle shown in Figure 3 and available thermodynamic functions of the reactions involved, we also obtained estimates for BDE of the neutral difluorinated [60]- and [70]fullerene molecules.

$$\Delta H^0_0(1) = EA(C_nF_2) - EA(C_n) + \Delta H^0_0(2)$$

The data used in calculations and the obtained values are presented in Table 4.

Electron Affinity Estimates of Monofluorinated [60]- and [70]Fullerenes. The lower bounds for electron affinities of monofluorinated [60]- and [70]fullerenes were estimated from the present experiments. The ions $C_{60}F^+$ and $C_{70}F^+$ were not registered in the mass spectra of systems 1−4. Taking into account the dynamic range of the instrument which is 10^5 in the electron impact mode and using experimental data from system 4, we estimated equilibrium constant values and enthalpy change values for reactions 16−18 (Table 2).

This subsequently leads to electron affinities of monofluorinated [60]- and [70]fullerenes (see Table 3). There is a satisfactory agreement with our earlier data for EA($C_{60}F$)[13] when monofluorinated species were first observed in the positive ion mass spectrum along with difluorinated species. The result points to the higher EA values for monofluorinated species by comparison with difluorinated molecules for both [60]- and [70]fullerenes.

The possibility of the formation of monofluorinated species through fragmentation/degradation of the higher fluorinated molecules under electron bombardment conditions must not be ruled out. In other words, generation of stable radicals with an odd number of fluorines at elevated temperature is not improbable. Furthermore in systems 1 and 4 no species with more than one attached fluorine was observed.

Since our first publication on monofluorofullerene anions,[13] new evidence for formation of the species with an odd number of fluorines attached to fullerenes in both gas phase[18] and in solution[19] has been reported.

Conclusions

In summary, the results presented in this paper show that addition of fluorine to a fullerene molecule or an ion is a thermodynamically favorable process. The C−F bond in fluorofullerene species with few fluorines attached appears to be much weaker than that of CF_4 (491 kJ/mol).[20] It is, however, stronger than was predicted theoretically,[21] and its value is very close to the C−F bond in the difluoroethane molecule (353 kJ/mol).[20] We did not find a significant difference in the energetics of the addition of fluorine to neutral molecules or to the negatively charged species.

The remarkable similarity of the trend in FA and EA in the higher fullerene series was observed; particularly, abnormally high FA for [74]fullerene should be noted. Further theoretical investigations are needed to understand and explain the observed regularities in terms of the electronic structure of the species. Finally, it has been successfully demonstrated that an application of the IME method to the new noninorganic objectives which in combination with the well-defined systems such as transition metal fluorides provided accurate measurements of the absolute thermodynamic quantities for the fluorinated fullerenes in the gas phase.

We are currently carrying out the measurements of fluoride anion exchange reactions of higher fullerenes and electron transfer reactions of endohedral metallofullerenes by the IME method.

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