Ab initio MO calculations and experimental observations on the reactivities of elemental fluorine and chlorine with graphite in the presence of HF

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Abstract

Ab initio MO calculations have been carried out on F_2–HF and Cl_2–HF complexes in order to shed light on the reactivities of elemental fluorine and chlorine with graphite The results show that the F_2–HF and Cl_2–HF complexes are stabilized by 10 50 and 5 2 kJ/mol respectively. A partial charge transfer from the halogen molecules (X_2) to HF occurs The X_2 molecules are polarized and the X atoms which are not hydrogen-bonded to HF carry a partial positive charge, making the complexes suitable for the dipole-induced dipole interaction with graphite Furthermore, the X_2 molecules interacting with HF can be regarded as easily polarizable, large "soft oxidants", facilitating the subsequent charge transfer from graphite HF plays a catalytic role both in intercalation and deintercalation processes In contrast with fluorine, the reaction of chlorine with graphite in the presence of liquid HF barely yielded a stage-two compound after a prolonged reaction time, which was in agreement with the results of calculation The lower reactivity of chlorine is attributed to the weaker interaction of Cl_2 with HF and its smaller oxidizing ability.

Introduction

In spite of a great number of graphite intercalation compounds (GICs) so far prepared, it is still difficult to predict theoretically which element or molecule will react with graphite to produce a GIC with desired properties and functionalities. Although the threshold value data of the physical properties, such as electron affinity [1] and vapour pressure, which a species to be intercalated ought to at least have, is being accumulated, the present situation still falls short of the systematic understanding of GIC reactions: how and why some reactions proceed and some do not. A typical example of this is the intercalation of halogens. Under normal conditions, despite their large electron affinities or oxidation enthalpies, fluorine and chlorine do not react spontaneously with

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graphite to produce stable GICs. Only bromine does so. Recently, it was found that the reaction of F_2 in the presence of HF easily produces a stage-one GIC [2, 3]. Deintercalation of metal fluorides takes place also in the presence of HF [4]. As for chlorine, some authors have reported the synthesis of C_xCl at −20 to −78 °C [5–7] using elemental chlorine alone. The products seem to be stable only under a Cl_2 atmosphere, and the staging and compositions remain unknown. In order to shed light on these problems, *ab initio* MO calculations on F_2–HF and Cl_2–HF complexes (which ought to play a role in intercalation processes) have been carried out. The calculations were made with the available highest level (MP4/6-31G**), and yielded stabilization energies larger than those obtained previously on F_2–HF [8] and Cl_2–HF [9]. Various reactions of chlorine with graphite have also been carried out.

Experimental

Intercalation reactions were carried out in a vacuum line made of Teflon and Kel-F. Chlorine gas (2 atm) was introduced into the reaction tube containing HOPG chips, and HF vapor in equilibrium with its liquid phase at 15 °C was added to it. In a similar way, the reaction of HOPG with a gaseous mixture of F_2, Cl_2 and HF, and the other reactions in the presence of liquid HF, were carried out.

Calculations

Calculations were carried out on the molecules F_2, Cl_2 and HF, and the complexes F_2–HF and Cl_2–HF, using the Gaussian 82 program system. The 6-31G** basis set was used. The structural optimizations were made by second-order Møller Plesset (MP2) perturbation theory, and the energy calculations by MP4 (SDTQ).

Results and discussion

Intercalation reactions

No reactions proceeded in the following gaseous systems: HOPG + Cl_2 (g); + F_2 (g); + Cl_2 (g) + HF (g); and + Cl_2 (g) + F_2 (g). The reactions were run for 14 days at 15 °C. The reaction of HOPG with Cl_2 (g) in the presence of liquid HF, however, produced an intercalation compound. (See Fig. 2, sample D, for its ESCA spectrum.) The X-ray diffraction pattern (XRDP) of the product indicated that the main phase was a stage-two GIC with $I_c = 6.61$ Å and $d_i = 3.26$ Å, but that some other higher-stage phases always co-existed. The results indicate that, in the reactions of graphite with elemental chlorine, HF does not act as a catalyst as effectively as in the cases with elemental fluorine [2, 3]. When elemental fluorine was added to this system, however, the reaction proceeded further quite rapidly.

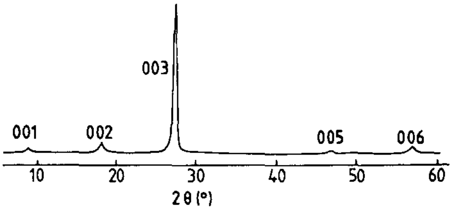

Fig. 1. X-ray diffraction pattern of the stage-two GIC obtained from the reaction of HOPG with Cl_2 (g), F_2 (g) and HF (g).

Figure 1 shows the XRDP of the dark-blue stage-two GIC made by the reaction of HOPG with a gaseous mixture of Cl_2, F_2 and HF. The value of I_c is 9.76 Å and d_i, therefore, is 3.06 Å. This value lies between those of the fluoride and chloride anions. The areas of F(1s) and Cl(2p) ESCA peaks indicate that the Cl:F molar ratio is always one, and the combination of the gravimetry with this molar ratio indicates its chemical composition to be $C_{10-12}ClF$. The binding energies of F(1s) (see Fig. 2, sample A) and C(1s) are 686.6 eV and 284.5 eV, respectively. Since the binding energies of F(1s) and C(1s), respectively, are close to that in LiF [10] and that of pristine HOPG, the compound is ionic, with the planarity of the layer with sp^2-hybridized carbon atoms being preserved. This compound is quite stable even in air and the XRDP has remained unchanged for at least 3 months. No stage-one compound of this type has been obtained so far.

The XRDP of the sample before completion of the reaction of Cl_2 in the presence of liquid HF and gaseous F_2 indicates that C_xHF_2 is formed as an intermediate product; C_xHF_2 is produced first and then chlorine intercalates in the form of $Cl_2 \cdots HF$. The ESCA spectra in Fig. 2 also support this mechanism. The more HF there is in the reaction system, the stronger becomes the peak at 688.5 eV, which can be attributed to the F atom in the $Cl_2 \cdots HF$ complex. This peak in sample A appears as a shoulder but becomes a main peak in samples C and D. The change from spectrum A to B indicates that only fluorine deintercalates when the sample is left in air for a long time. The apparent contradiction between the results of ESCA and XRDP (*i.e.* a major change from A to B in Fig. 2 on one hand and the persistence of the same XRDP on the other) is attributed to the fact that ESCA techniques deal with surface properties of a sample while the X-ray method reflects bulk properties.

Calculations on the F_2–HF complex

Figure 3a shows the optimized structure of the F_2–HF complex. The relevant calculation results are given in Tables 1 and 2. The stabilization energy ΔE of the complex F_2–HF was -10.50 kJ/mol and the hydrogen bond distance $R(F_2\text{–}HF) = 2.0506$ Å. Compared with our preliminary work where the structural optimization was made by the RHF (Restricted Hartree–Fock) method and the energy calculation by MP2, the bond

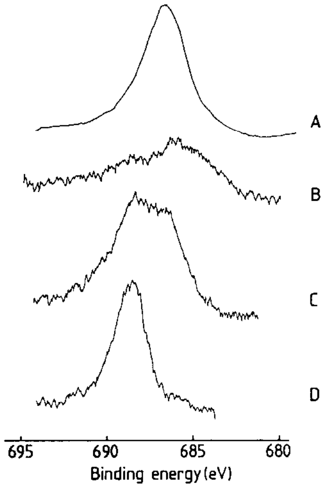

Fig. 2. F(1s) ESCA spectra: (A) stage-two GIC obtained by the reaction of HOPG with Cl_2 (g), F_2 (g) and HF (g) shown in Fig. 1; (B) after 3 months' exposure of sample A to air; (C) stage-two GIC obtained by the reaction of HOPG with Cl_2 (g) and F_2 (g) in the presence of liquid HF; (D) GIC obtained by the reaction of HOPG with Cl_2 (g) in the presence of liquid HF.

distance of F_2 is shorter and the stabilization energy larger by 2 kJ/mol, suggesting an important electronic correlation energy in the F_2–HF system. The stabilization energy obtained here is also larger than that (−9.15 kJ/mol) obtained by Reed *et al.* [8]. Although the hydrogen bond is a little longer and ΔE smaller compared with the case of the typical hydrogen bonding system of the linear $(HF)_2$ dimer [R(HF–HF) = 1.95 Å, $\Delta E = -19.36$ kJ/mol] [11], the F_2–HF complex is, nevertheless, significantly stabilized.

R(F–F) in the complex is larger than that in an isolated F_2 molecule by 0.0036 Å. A partial charge transfer from F_2 to HF occurs. As is shown

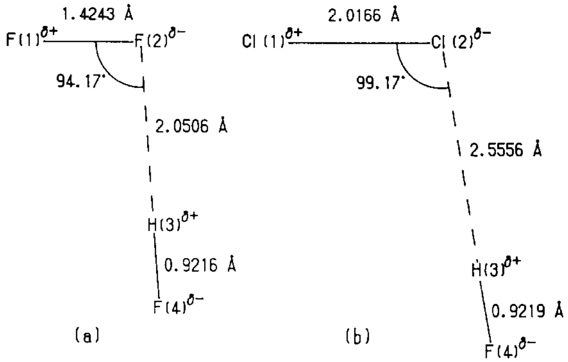

Fig. 3. (a) Optimized structure of the F_2-HF complex; (b) optimized structure of the Cl_2-HF complex.

TABLE 1

Optimized geometries and energies

System	Bond length (Å)			Dipole moment	Total energy	ΔE[a]	
	R(X–X)	R(H–F)	R(X_2–HF)	(Debye)	(A.U./10^3 mol)	(10^3 A.U./mol)	(kJ/mol)
F_2	1.4207				−0.19905115075		
Cl_2	2.01510				−0.91920440285		
HF		0.9210		1.9793	−0.10020142975		
F_2–HF	1.4243	0.9216	2.0506	2.2489	−0.29925655643	−3.984	−10.50
Cl_2–HF	2.0166	0.9219	2.5556	2.2974	−1.0194077974	−1.965	−5.2

[a] $\Delta E = E(X_2\text{–HF}) - E(X_2) - E(\text{HF})$

TABLE 2

Total atomic charges, q

System	Atom[a]	q
F_2–HF	F(1)	8.9727
	F(2)	9.0106
	H(3)	0.6072
	F(4)	9.4095
Cl_2–HF	Cl(1)	16.971532
	Cl(2)	17.021477
	H(3)	0.660465
	F(4)	9.406526
HF	H(1)	0.6029
	F(2)	9.3971

[a] See Fig. 3 for the numerical labels.

in Fig. 3a, the fluorine molecule is polarized and the F atom which is not hydrogen-bonded to HF carries a partial positive charge, making the complex suitable for the dipole-induced dipole interaction with graphite. Furthermore, by analogy with the HSAB (hard and soft acids and bases) principle, the F_2 molecule interacting with HF as a whole can be regarded as a more easily polarizable, large 'softer oxidant' than an isolated F_2 molecule, facilitating the subsequent charge transfer from graphite, which acts as a 'soft reductant'. This rule seems to apply to the reaction of graphite with alkali metals: graphite, which is 'amphoteric', acts this time as a 'soft oxidant' favouring interaction with 'softer reductants' like Cs, Rb and K. However, the oxidizing or reducing ability of the reagents must also be taken into consideration.

When the energy levels are examined, it is noticed that not only is the HOMO energy (−0.6240 Hartree) of the F_2–HF system much higher than that (−0.6421 Hartree) in molecular F_2, but also the energy difference between LUMO and HOMO is much smaller (0.7599 Hartree for F_2–HF and 0.8098 for F_2). This result also suggests that F_2 interacting with HF possesses a higher reactivity.

Summarizing the above observations, when HF co-exists in the graphite/F_2 reaction system as an impurity or a catalyst, the following intercalation reaction processes can take place:

$$\begin{array}{lll}
C_{2x} + HF & \longrightarrow C_{2x}\cdots HF & \text{(adsorption of HF)} \\
\quad + F_2 & \longrightarrow C_{2x}(F^{\delta+}\text{–}F^{\delta-}\cdots HF) & \text{(adsorption and polarization of } F_2\text{)} \\
 & \longrightarrow C_{2x}{}^{+}F^{-}\cdots FHF & \text{(charge transfer from graphite)} \\
 & \longrightarrow C_{2x}{}^{2+}F^{-}\cdots FHF^{-} & \text{(charge transfer from graphite)} \\
 & \longrightarrow 2C_{x}{}^{+}F^{-} + HF & \text{(formation of an ionic fluoride GIC)}
\end{array}$$

To support the above mechanism, we have the following observation [4]: $C_{24}SnF_5$, which was produced by substitutional intercalation in an HF solution of SnF_4 bubbled with F_2 [12], is stable up to 150 °C in an F_2 atmosphere. In a gas mixture of HF and F_2, however, deintercalation proceeds to completion. HF plays an important catalytic role in the deintercalation process, interacting with F_2 and the intercalant.

Calculations on the Cl_2–HF complex

The stabilization energy ΔE of the complex Cl_2–HF was −5.2 kJ/mol, which is larger than that (−4.33 kJ/mol) obtained by Rendell *et al.* in the same geometry [9]. This value is about half of that in the F_2–HF system, indicating a stronger interaction in the latter. The dipole moment, however, is comparable to that in F_2–HF, with an accompanying partial charge transfer from Cl_2 to HF. As was the case in the F_2–HF complex, the Cl–Cl bond in the complex, is polarized to some extent. Although the interaction of Cl_2 with HF is weaker than F_2, considering the sizes of F_2 and Cl_2, the Cl–Cl interacting with HF is not necessarily less ‘soft’ than the F_2–HF complex. Therefore the facility with which F_2–HF and Cl_2–HF form an intercalation compound ought to be governed by the combination of the oxidizing ability and the ‘softness’ of the reagents.

Conclusions

The present calculation results on the intercalation of halogens, together with the experimental observations, indicate that electron affinity or oxidation enthalpy is not necessarily the only factor for acceptor-type GIC formation. The oxidizing ability being kept constant, the larger the electron sphere and the greater the polarizability of an element (*i.e.* the ‘softer’ the element), the easier it can form a GIC. Therefore, the experimental fact that elemental fluorine does not spontaneously intercalate under normal conditions reflects the peculiarities of fluorine with the smallest electron sphere and, therefore, a very small polarizability.

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