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Affinity of Xenon(II) and Carbon in the (Heptafluorocyclohexa-1,4-dien-1-yl)xenonium Ion for Fluoride Ion and Acetonitrile

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Abstract—The results of B3LYP&PCM quantum-chemical calculations confirmed the possibility for formation of fluoro(heptafluorocyclohexa-1,3-dien-1-yl)xenon and (octafluorocyclohex-3-en-1-ylidene)xenon from (heptafluorocyclohexa-1,4-dien-1-yl)xenonium in liquid acetonitrile. The Xe(II) and C^2 atoms in the cation are characterized by a strong affinity for fluoride ion, but the Xe(II) atom binds acetonitrile molecule. The addition of F^- to C^2 in $[XeC_6F_7]^+$ is more favorable (by 6 kcal/mol) than replacement of the fluorine atom on Xe(II) by MeCN molecule. The charge on the xenon atom in (octafluorocyclohex-3-en-1-ylidene)xenon is small, the Xe–C bond is weakened, and its cleavage leads to ring contraction to perfluoro(3-methylidenecyclopent-1-ene).

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Frohn and Bardin [1] studied the chemical properties of (heptafluorocyclohexa-1,4-dien-1-yl)xenonium hexafluoroarsenate(V) and found that its reaction with sodium fluoride in acetonitrile is accompanied by transformation of the six-membered ring into five-membered. This unexpected result was rationalized by the authors [1] in terms of preferential attack by the hard anionic nucleophile (fluoride ion) on the hard electrophilic C^2 atom rather than on the soft electrophilic Xe(II) center in (heptafluorocyclohexa-1,4-dien-1-yl)xenonium (**I**). Therefore, (octafluorocyclohex-3-en-1-ylidene)xenon (**III**) is formed instead of fluoro(heptafluorocyclohexa-1,4-dien-1-yl)xenon (**II**) structurally related to fluoro(pentafluorophenyl)xenon [2–4]. Compound **III** then loses the xenon atom to give the corresponding cyclic carbene, and rearrangement of the latter leads to the formation of perfluoro(3-methylidenecyclopent-1-ene) (**IV**) as final product [1, 3]. On the other hand, the same authors obtained fluoro(pentafluorophenyl)xenon in a good yield (70%) by low-temperature reaction of (pentafluorophenyl)xenon salt and tetramethylammonium fluoride in methylene chloride [2, 3]. The fluoro(pentafluorophenyl)xenon molecule contains a chemical bond between the hard fluoride ion and xenonium.

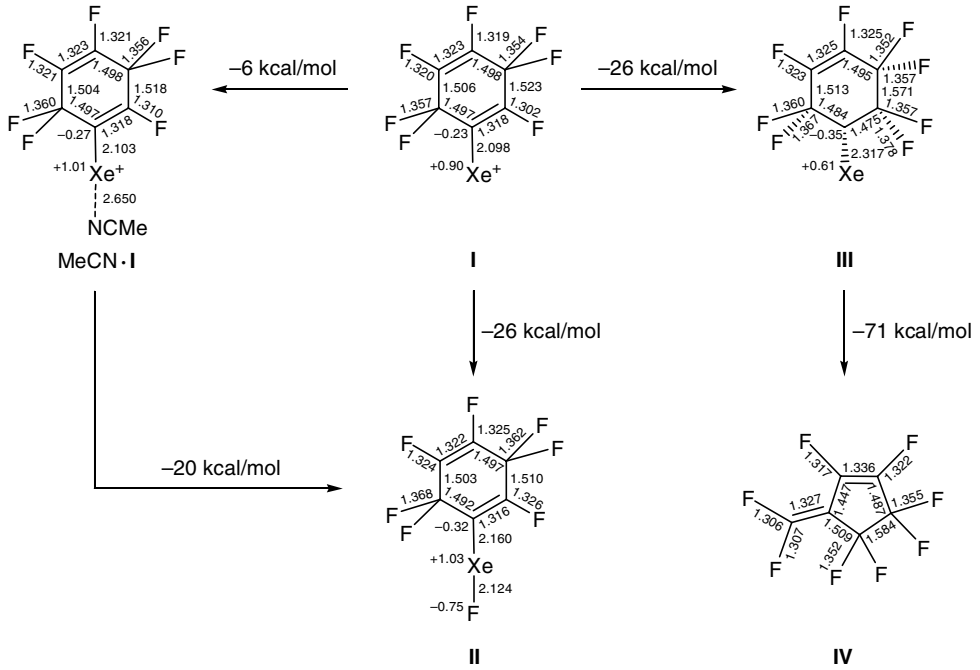
In the present work we confirmed the possibility for formation of both molecules **II** and **III** and cationic adduct MeCN·**I** in liquid acetonitrile by quantum-chemical methods. The corresponding energy minima and vibration wave numbers were determined by the C-PCM/B3LYP/(6-311G** & Xe 3-111G*) calculations. A formal dissociation energy of 7 kcal/mol was obtained for the adduct of cation **I** with acetonitrile molecule coordinated at the Xe(II) atom. This value is the difference between the energies of solvated particular components and that of the adduct.

Strong electrostatic effect of cation **I** on the coordinated acetonitrile molecule leads to increase of the C≡N vibration frequency by 1.1% and increase of the calculated intensity of the corresponding IR band by a factor of 3.47. Analogous results were obtained by us previously for the adduct of (pentafluorophenyl)xenonium with acetonitrile molecule [4]. With a view to verify these results we performed calculations of the solvate complex $(MeCN)_4Li^+$ in acetonitrile (for which spectroscopic data are available) and found that the vibration frequency for molecules in the first coordination sphere increases by 1.0% (by 1.2% in the IR spectrum [5]) and that the intensity increases by a factor of 2.3 (against 3.1 [5] and 3.4 [6] in the experimental spectra).

Acetonitrile molecule interacts with the carbon atoms in cation **I** in the nonspecific mode: the formal energy of dissociation of the corresponding hypothetical adducts in liquid acetonitrile turned out to be equal to zero.

Using the C-PCM/B3LYP/[6-311G($3d_5f_7$,p) & Xe 3-111G(d_5)] procedure, which was applied previ-

Scheme 1.



ously to calculate structural parameters and properties of solvated (pentafluorophenyl)xenonium and fluoro-(pentafluorophenyl)xenone [4], we have refined structural parameters of the above molecules and cationic species in acetonitrile and then calculated again their energies (with account taken of zero-point vibration energies determined previously) and charges on atoms in terms of the PCM/B3LYP/[6-311G++($3d_5f_7$,p) & Xe 3-111G($3d_5$)] procedure. Unfortunately, no perfectly correct and universal method for calculation of charges on chemically bonded atoms has been proposed so far. Disadvantages of the existing methods were discussed in many publications (see, e.g., [7]). Nonplanar equilibrium nuclear configurations of the compounds under study and the presence of a polarizable medium (MeCN) prompted us to apply the natural population analysis (NPA) method [8]. Scheme 1 shows the calculated structures with charges on the Xe atom and carbon atom attached thereto (a.u.; calculated by the NPA method) and bond lengths (Å).

The C–Xe^+ bond in adduct MeCN·**I** (2.103 Å) is slightly longer than the corresponding bond in the adduct formed by aromatic (pentafluorophenyl)xenonium (2.088 Å, as calculated for solution [4], and 2.092 Å according to the X-ray diffraction data [9]). The interatomic distance $Xe^+\cdots N$ in adduct MeCN·**I** (2.65 Å) approaches those found for the adduct with aromatic cation (2.66 Å for solution [4] and 2.68 Å in crystal [9]).

The energies of formation of molecules **II** and **III** from cation **I** and fluoride ion, calculated in terms of the polarizing continuum model (PCM), turned out to be equal to 26 kcal/mol, but the energy released upon replacement of the MeCN molecule in adduct MeCN·**I** by fluoride ion is smaller by 6 kcal/mol then the energy released upon addition of F^- to C^2 in cation **I**. Thus, the energy preference of intermediate **III** is determined by the affinity of xenon for acetonitrile molecule. The refined formal dissociation energy of adduct MeCN·**I** (6 kcal/mol) is lesser by 1 kcal/mol than the value obtained previously using a smaller basis set.

The single Xe–F bond in molecule **II** is longer by 0.1 Å than in the XeF_2 molecule, but it is so strongly polar that compound **II** may be regarded as a contact ion pair. The C–Xe bond in molecule **III** is longer by 0.214 Å than the corresponding bond in initial adduct MeCN·**I**, and the charge on the xenon atom is appreciably smaller. Therefore, compound **III** fits better the singlet exciplex structure rather than ylide structure with a ionic–covalent $=C^-–Xe^+$ bond [1, 3]; its decomposition is accompanied by liberation of xenon and rearrangement of the six-membered ring into perfluoro-(3-methylidenecyclopent-1-ene): **III** → **IV** + Xe + 71 kcal/mol. The C^2–C^3 bond being broken in intermediate **III** is shorter than the anomalously long C^5–C^6 bond that is conserved in the rearrangement. A specific character of the reaction under study is that it is

initiated by fluoride ion, unlike thermal or photochemical Wolff rearrangement.

The calculations were performed with the use of GAUSSIAN software package [10].

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