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High level *ab initio* thermochemistry of XeF radical

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ABSTRACT

Thermodynamic characteristics of XeF_2 stepwise defluorination reaction have been studied using sophisticated methods of quantum chemistry. The set of standard enthalpies of formation for the XeF_2-related intermediates (radicals, ions) was obtained using approximation of coupled clusters level of theory [CCSD(T)/complete basis set extrapolation] with Peterson's effective core potential correlation consistent basis sets for Xe. The standard enthalpy of formation for xenon monofluoride radical was determined to be $\Delta_f H^\circ(XeF\cdot) = 15.4\,\text{kcal mol}^{-1}$ (298 K). The radical is formed in the first step of XeF_2 homolytic decomposition which requires $59.7\,\text{kcal mol}^{-1}$. The second step ($XeF\cdot$ dissociation) is characterized by an extremely low binding energy (*BDE* (XeF) = $3.1\,\text{kcal mol}^{-1}$) explaining the high fluorinating potential of the xenon difluoride. An interpretation of low $XeF\cdot$ stability was given in terms of MO – AO correlation diagrams. It was shown that the electronic structure of $XeF\cdot$ radical may be described as combination of two main configurations, the first of them has a canonical set of MOs with single-occupied HOMO of antibonding character, whereas the second configuration is characterized by low-lying SOMO with main contributions from 5S AO of Xe and $2p_z$ AO of fluorine.

1. Introduction

Xenon difluoride (XeF_2) is widely used in fundamental and applied research as fluoro-oxidant [1] in organic and inorganic synthesis of fluorine-containing compounds [2–5], as a source of fluorine for chemical and excimer lasers [6], as a component of cathode materials of chemical power supplies [7]. Studies of XeF_2 unique properties in non-aqueous solvents have made it possible to develop and refine many positions of fluorine chemistry, theory of reactivity, coordination chemistry, *etc.* [8–11].

The beginning of the third millennium was marked by a sharp increase of interest in the compounds of noble gases, which the well-known chemist K.O. Christie called "the renaissance of the chemistry of noble gases" [12]. In particular, XeF_2 has been used in various fields of nanotechnology [13]: in the preparation of carbon nanostructures and their derivatives – fullerene, graphene, graphane and fluorographene [14,15], in ion-plasma etching of semiconductors [16], namely, in selective gas-phase etching of silicon and other materials used for microelectromechanical systems [17,18]. It became possible to synthesize new regular and coordination compounds of many elements, including transition metal fluorides in higher oxidation states [19–23] with use of XeF_2. Fluorine-18 labeled XeF_2 has been used in the first regioselective fluorination of the most commonly used ^{18}F-labeled radiopharmaceuticals for positron emission tomography [24].

It was found in our laboratory that xenon release during XeF_2 reduction by water is accompanied by chemiluminescence [25]. It was believed that a highly active XeF radical – one of the key intermediates in the noble gas halides chemistry – is generated during XeF_2 reaction with water [26]. The radical was first registered upon γ-ray destruction of XeF_4 at low temperature [27]. It should be noted that many *RedOx* reactions XeF_2 with uranium (IV), (VI), organometallic compounds as well as with lanthanide ions are also chemiluminescent [28–35]. The chemiluminescence spectrum of the reactions is located in a wide range area – from UV to IR. However, not all emitters are uniquely identified, and XeF radical was considered as a possible candidate to emit a light. Reliable emitter identification in the various reactions of XeF_x compounds ($x = 2 \div 6$) as well as determination of mechanism of excited states generation requires trustworthy thermodynamic characteristics of short-lived intermediates. In view of this, the thermochemistry of $XeF\cdot$ radical is of particular interest.

Up to day the investigation of $XeF\cdot$ radical has been focused mainly on the spectral properties, not the chemical transformations. To understand the latter, the nature and strength of XeF bond is needed to be described. The known information on the $XeF\cdot$ thermochemistry is contradictory: the XeF bond strength varies from 3 [36,37] (derived from emission spectra of $XeF\cdot$) to $10\,\text{kcal mol}^{-1}$ [38] (estimated from the reaction rates of xenon fluorides with oxides of nitrogen by fast-reaction cell method using mass spectrometry). The inconsistence in experimental data is apparently due to low bond dissociation energy and requires a more reliable estimation of $XeF\cdot$ energetics. Despite the

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Table 1
CCSD(T)/CBS energies for reference reactions (kcal mol^{-1}).

Reaction	ΔE_{CBS}	ΔE_{ZPE}[a]	ΔE_{H}[a]	ΔE_{SO}[b]	ΔE_{R}[a,c]	$\Delta_r H^\circ_0/\Delta_r H^\circ_{298}$ (calc)	$\Delta_r H^\circ_0/\Delta_r H^\circ_{298}$ (exp)
$XeF^- \rightarrow Xe + F^-$	6.71	−0.18	0.28	0.00	0.00	6.54/7.00	–
$XeF\cdot \rightarrow Xe + F\cdot$	3.26	−0.28	0.25	0.39	−0.03	2.56/3.10	3.04 [36]/10 [38]
$XeF^+ \rightarrow Xe\cdot^+ + F\cdot$	52.71	0.00	−0.13	10.43	−0.02	42.26/42.13	–/44.95 [68]
$XeF_2 \rightarrow XeF\cdot + F\cdot$	60.93	−1.60	−0.64	0.39	−0.17	58.77/59.74	60.37 [36]/60.2
$XeF_2 \rightarrow Xe + 2F\cdot$	64.19	−1.89	−0.39	0.77	−0.20	61.33/62.83	62.24 [68], 63.42 [69]/–
$XeF_2\cdot^+ \rightarrow XeF^+ + F\cdot$	10.35	−1.02	−0.33	0.39	−0.03	8.91/9.61	–
$XeF_2\cdot^+ \rightarrow Xe\cdot^+ + 2F\cdot$	63.06	−1.95	−0.45	10.81	−0.05	50.24/51.75	–
$F_2 \rightarrow 2F\cdot$	38.15	−1.32	−0.46	0.77	−0.01	36.06/36.92	36.76 [58]/37.76 [58]
$F_2 + 2\bar{e} \rightarrow 2F^-$	−119.60	−1.32	−0.46	0.00	0.43	−120.49/−119.64	−119.82 [58]/−121.93 [58]
$Xe\cdot^+ + \bar{e} \rightarrow Xe$	−289.60	0.00	0.00	−10.04	0.00	−279.55/−279.55	279.72 [58] /281.20 [58]

[a] Computed with basis set of quadruple ζ quality.
[b] Accounted from weighted average of the spin-orbit splittings for the lowest energy state.
[c] Implemented on the level of Douglas-Kroll-Hess second order scalar relativistic approximation.

accurate and thorough study on xenon fluorides thermochemistry was recently performed [39–41], the thermochemical characteristics of the $XeF\cdot$ are not dealt with in these publications. Thus, in present work high-level *ab initio* quantum chemical computations were performed to estimate thermodynamic and electron density characteristics of a highly active intermediate of XeF_2 decay – $XeF\cdot$ radical.

2. Computational procedures

We used complex approach described in references [39,40] to predict the thermodynamic properties of XeF_2 and species involved in its dissociation based on molecular orbital theory using coupled cluster methods [42–44] with Single, Double and non-iterative Triple excitations CCSD(T) [45,46]. The standard correlation-consistent (Dunning) aug-cc-pV*n*Z, with n = D–Q, basis sets [47–51] were used for F. Systematically converged basis sets (aug-cc-pV*n*Z-PP, n = D–Q) with relativistic small core pseudopotentials [52,53] were used for Xe. Open shell unrestricted (U) wave function [UCCSD(T)] was used for $XeF_2{}^+\cdot$, $XeF\cdot$, $F\cdot$, and $Xe^+\cdot$ [54]. Our complete basis set (CBS) extrapolation technique is based on mixing exponential and Gaussian functions as presented by expression (1) [50]:

$$E_{total,n} = E_{CBS} + B\cdot\exp(-(n-1)) + C\cdot\exp(-(n-1)^2), \qquad (1)$$

with n = 2 (double ζ), 3 (triple ζ), and 4 (quadruple ζ) giving E_{CBS}. Reaction heat effect was estimated using the following equation described in Refs. [55–57]:

$$\Delta_r H^\circ = \Delta E_{CBS} + \Delta E_{ZPE} + \Delta E_H - \Delta E_{SO} - \Delta E_R, \qquad (2)$$

where ΔE_{CBS} is a CBS-extrapolated change of total energy in a reaction; ΔE_{ZPE} is a difference in zero-point energies of products and reactants; ΔE_H – thermal correction for reaction enthalpy; $\Delta E_{SO}/\Delta E_R$ are correction terms calculated using spin-orbital (SO) energies and relativistic (R) contributions for all participants of a reaction, correspondingly. The values of ZPE and thermal correction to enthalpy were obtained by vibrational frequency calculation with basis set of quadruple ζ quality. Electronic spin splitting correction to CBS energy was accounted from atomic energy levels and the spin-orbit splittings taken from Refs. [58] as a weighted average of the splittings for the lowest energy state. The values of E_{SO} are equal to 0.39 and 10.04 kcal mol^{-1} for fluorine radical and xenon cation, correspondingly. Spin-orbital correction estimated for $XeF\cdot$ in CASSCF(15,9) approximation is small enough to be neglected in the heat effect calculations. Relativistic correction[1] was implemented on the level of Douglas-Kroll-Hess second order scalar relativistic approximation [59–62] with quadruple ζ basis set.

All the presented structures correspond to minima on potential energy surface: imaginary vibrational frequencies have not been detected in hessian calculations. Diagnostics for determining the quality of single-reference electron correlation was carried out by standard technique (T1 diagnostic of Lee and coworkers [63] at the CCSD level). Calculations were carried out using Gaussian 09, Revision D.01 program package [64]. Multi-configuration SCF calculations were performed in Firefly 8.2.0 [65,66]. Visualization and analysis of molecular orbitals (MO) were performed using ChemCraft [67].

3. Results and discussion

Quantitative analysis of the thermochemistry of XeF radical requires accurate energies of both the target structure and related particles as well as processes with their participation to confirm the adequacy of the calculated data. All quantities required for calculation of standard enthalpies for selected chemical transformations are summarized in the Table 1. Calculated as well as experimental heats of formation of the species involved in XeF_2 decomposition are collected in Table 2. MO – AO correlation diagrams of XeF^-, XeF^+, $XeF\cdot$ and XeF_2 are presented in Figs. 1–3.

As it may be seen from Tables 1 and 2, our CCSD(T)/CBS results correlate well with the available experimental values which include enthalpies of formation and atomization, ionization potentials and geometry. This makes it possible to use MO – AO correlation diagrams constructed on the base of present quantum chemical calculations in explaining of the stability and reactivity of compounds under study. According to experimental [36] and theoretical data stepwise homolytic dissociation of XeF_2 is characterized by significant decreasing of bond dissociation energy (*BDE*) of the only remaining Xe—F bond as compared to that for first fluorine atom abstraction. Indeed, $BDE_{FXe\text{-}F}$ is equal to $58.77_{0\,K}/59.74_{298\,K}$ kcal mol^{-1} while XeF_2 atomization energy is $61.33_{0\,K}/62.83_{298\,K}$, *i.e.* $BDE_{XeF} = 2.56_{0\,K}/3.10_{298\,K}$ kcal mol^{-1} at CCSD(T)/CBS level of theory (see Table 1). These results give an opportunity to calculate the formation enthalpy for $XeF\cdot$ radical, which was found to be 15.4 kcal mol^{-1} at 298 K. The phenomenon of extreme non-equivalence of XeF bond strengths can be associated with the different character of bonding between Xe and F atoms in XeF_2 and $XeF\cdot$ and can be traced using electronic structures of XeF_2 and $XeF\cdot$ as it is shown on the MO diagrams presented on Figs. 2–3. The MO-AO correlation diagrams for XeF^- and XeF^+ were also constructed for comparative purposes. As may be seen from Fig. 1(a) the anion species characterizing by double occupancy of σ_z*-antibonding orbital and formally zeroth bond order has very weak Xe—F bond (7.0 kcal mol^{-1}) with interatomic distance of 2.95 Å. On the contrary, the cation (see Fig. 1(b)) is qualitatively different from the anion by the presence of vacant σ_z*-antibonding orbital and formally half bond order which makes Xe—F bond to be stronger by 35 kcal mol^{-1} and shorter by 1.085 Å. At first glance, $XeF\cdot$ radical should demonstrate intermediate

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[1] Relativistic correction to CBS energy obtained using perturbation theory based on the usual *mass-velocity* and *one-electron Darwin* terms are given for some atoms in Supplementary Information section for comparison.