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A theoretical study of stabilities, reactivities and bonding properties of XKrOH (X= F, Cl, Br and I) as potentially new krypton compounds using coupled cluster, MP2 and DFT calculations

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CCSD, CCSD(T), MP2, CAM-B3LYP and WB97XD calculations were employed to disclose the conceivable existence of new noble gas molecules, XKrOH (X = F, Cl, Br and I). The calculations were used to present the optimized geometries, vibrational modes, molecular properties, thermodynamic and 10 kinetic stabilities and atomic descriptions of these molecules. IKrOH and BrKrOH molecules showed two X^- and $KrOH^+$ parts, while in FKrOH and ClKrOH, they could be presented as XKr^+ and OH^-. Two decomposition routes (two-body and three-body) were proposed, showing high exothermic reactions especially for the two-body decomposition. However, their decomposition rate constants were small and all molecules had high kinetic stabilities. Comparing relative stabilities and using heats of formations and 15 isodesmic reactions showed that the FKrOH and IKrOH were the most stable and the least stable structures, respectively. Moreover, natural bond orbital (NBO) calculations were used to obtain atomic charges, hybridizations and intermolecular interactions via second-order perturbation energies and the bonding properties of XKrOH molecules were studied by atom in molecule (AIM) calculations. Both of these calculations confirmed the nature of the ionic parts of the molecules and presented a clear picture of 20 their bonding properties. The reactivity parameters, as obtained from population analyses, also showed that the reactivities were increased and stabilities were decreased from FKrOH to IKrOH.

Introduction

The noble (or rare) gases, discovered in the 1890s by Ramsay and co-workers, were for a long time assumed to be chemically 25 inactive. In 1962, Bartlett synthesized "Xe⁺PtF₆⁻", the first stable noble gas compound, and proved that rare gases seemed to be less inert than what it was suggested.[1] Since then, numerous compounds consisting of noble gases have been prepared and structurally characterized.[2-5] Now, our knowledge of the bonding 30 and properties of the noble gases has significantly been expanded and a large number of studies have been reported in this area. For example, a noble gase can make bond with another noble gas,[6] proton,[7] sulfur,[5] selenium,[8] mercury,[9] gold[10] and oethr atoms.[11-15] The most important issue for noble gas compounds is related to 35 their stabilities. Based on the fundamentals of chemistry[16] and the fact that the valence layer of the noble gases is full of electrons (their octet is complete), they do not tend to participate in bonding with other atoms to make molecules. However, noble gases with a larger atomic number, such as xenon and krypton,[17] 40 have more remarkable tendencies to participate in chemical bonds because they have less ionization potential than the other noble gases.[18-20] In this line, krypton is less famous than xenon in making stable molecules. This is due to the difference in the ionization potentials of krypton (14.00 eV) and xenon (12.13 45 eV).[21] However, many krypton compounds have been studied

such as (HKrX),[22-25] KrF₄,[26] KrF₂[27] and FKrCF₃, FKrSiF₃, and FKrGeF₃.[28] These primary studies have suggested that real chemical bonds, rather than simple van der Waal's forces, were possible for noble gas atoms.[29] One of the older known krypton 50 containing compounds is HKrCN, which has been studied using both computational and experimental methods.[3] In addition, some researchers characterized the first "organokrypton" molecules, HKrCCH and HKrC₄H, by both computational and experimental methods.[30-31] Most of these reported works have shown the 55 stability of molecules containing krypton. Although some krypton containing compounds have been prepared successfully, isolation, preparation and study of new compounds in this category by experimental methods is difficult. Therefore, computational techniques were mostly used to study these, especially for 60 unknown molecules. By using theoretical methods, the bonding, formation, stability and properties of these compounds could be anticipated.[32,33] For example, the insertion of krypton into water to form HKrOH was first predicted theoretically.[34] This study also determined the two-body dissociation way of HKrOH to Kr 65 and H_2O with a barrier of about 0.52 eV. It was later found that the three-body dissociation to H + Kr + OH with a barrier of about 0.15 eV was lower than that of the previous report.[35]

One possible way for the reaction of noble gases is the insertion of them into hypohalous acids.[36] In one way, this insertion can 70 produce H-Ng-OX. In this line, HXeOX[37] and HKrOX[38] have

been studied theoretically, proposing that these molecules are stable. However, no report on the insertion of krypton in hypohalous acids in another way to produce XKrOH has been observed while the preparations and stabilities of HKrCl[29] and HKrOX[37] have been reported. These reports have shown that krypton can make covalent bonds with halogen (Kr-X bond) and oxygen (Kr-O bond) to produce stable molecules.[39,40] Therefore, it is possible to gather these two bonds in one molecule and make XKrOH. In addition, we have recently reported a theoretical study of XXeOH as a xenon analog of this molecule.[41] Therefore, we continued our attempts in theoretical chemistry,[42-44] to study the structure, bonding, stability and other properties of XKrOH so that it would give us important information on krypton compounds and expand our knowledge of krypton chemistry.

In the present work, first, we found the bonding and molecular properties of XKrOH such as optimized structural parameters and vibrational frequencies. Then, more information about the bonding properties, hybridizations and atomic charges, and second order perturbation energies was found using NBO calculations. Finally, the energy profiles of the decomposition way for XKrOH and heats of formation and relative stabilities, as obtained from isodesmic reactions, were derived from the calculations. The following sections will discuss the results.

Methods

Gaussian 09 program package[45] was used to optimize the structure of XKrOH molecules and calculate the molecular properties. Calculations were carried out using density functional theory[46,47] (DFT, two CAM-B3LYP[48] and WB97XD[49] methods have been used), Moller-Plesset theory (MP2)[50] and coupled cluster theory (CCSD)[51] in combination with 6-311++G**[52] and Aug-CC-PVTZ[53] basis sets for all atoms except iodine. For iodine, an effective core potential (ECP) basis set (LANL2DZ) was used. In addition, to obtain correct barrier energies and stability values, all energy values were corrected using the results of CCSD(T)/Aug-CC-PVTZ single point calculations. The absence of imaginary frequency verified that the structure was true minima at its respective levels of theory. The structure of transition states was optimized by applying Schlegel's synchronous-transit-guided quasi-Newton (QST3) method, which was started from the fully optimized structure of XKrOH and finished on the fully optimized structure of products. The transition states were confirmed by frequency calculations. Additionally, intrinsic reaction coordinate (IRC) calculations proved that each reaction linked the correct products with the reactants. Rate constants were calculated by canonical transition state theory using Eyring equation.[54] The results of frequency calculations were used after applying an appropriate scaling factor.[55] NBO analysis of all structures was done using NBO[56] program as implemented in the Gaussian program package. NBO calculations are known as useful tools to calculate molecular properties such as atomic charges, atomic hybridizations and the interactions between orbitals (second-order perturbation energies) with high precision. AIM analyses were performed using AIM2000 program.[57] NBO has presented useful information on intermolecular interactions and characterization of bonds through the analysis of electron density.[58] Both NBO and AIM calculations have been performed using CCSD calculations. Atomization energy method[59] was used in the calculation of ΔH^o_f and ΔG^o_f for XKrOH at all theory levels; also, isodesmic reactions[60,61] were used to estimate the relative stabilities of XKrOH when the halogen atom was changed. To examine the reactivities, the chemical potential (μ), chemical hardness (η), global softness (S) and electrophilicity index (ω) were calculated as defined in equations 1-4, according to Koopman's theorem.[62,63]

$$\mu= (E_{LUMO}+E_{HOMO})/2 \qquad \text{(Eq. 1)}$$
$$\eta= (E_{LUMO}-E_{HOMO})/2 \qquad \text{(Eq. 2)}$$
$$S=1/\eta \qquad \text{(Eq. 3)}$$
$$\omega= \mu2/2\,\eta \qquad \text{(Eq. 4)}$$
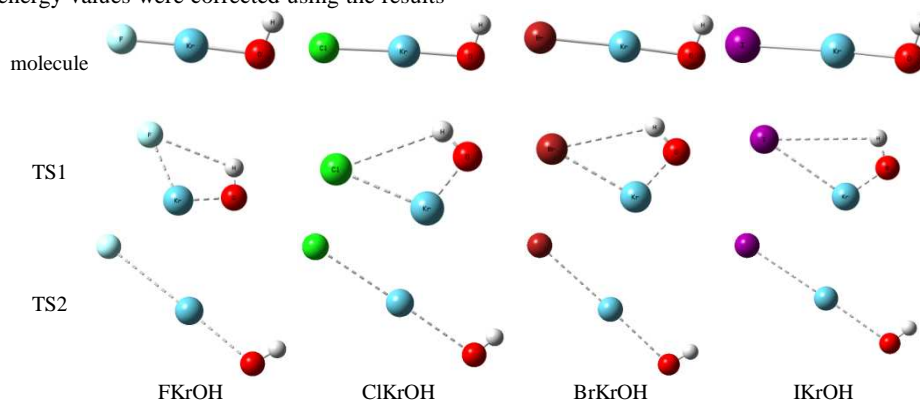
Fig. 1 Graphical representation of the optimized structures for XKrOH molecules and their transition states for decomposition reactions extracted from CCSD/Aug-CC-PVTZ calculations

Results and discussion

Structural parameters

After the optimization of all XKrOH (X=F, Cl, Br, I) structures, their structures, as optimized without any symmetry restriction or pre-defined conformational structures, are shown in Fig. 1, along with the optimized structures of transition states to be discussed in the next section. In addition, molecular parameters such as bond lengths, bond angles and dihedral (torsion) angles were obtained from these optimized structures. The results are listed in Table 1 for molecules and transition states.

As shown in Table 1, all molecules were nearly planar with X-Kr-O-H dihedral angle being almost 180.0 degrees. The X-Kr-O

angles were between 177.8-179.0 degrees, showing the linear arrangement of atoms around krypton with small deviation (maximum 1.2 degrees). Kr-O-H angles were in the normal range, between 103.2-104.5 degrees. For O-H bond lengths, a few
5 cases of increase could be observed from FKrOH to IKrOH and in all structures, it was between 0.963-0.964 Å. Despite the previous parameters, Kr-O bond lengths were affected by changing halogen atom from 1.910 Å in FKrOH to 2.049 Å in IKrOH. It seems that by the increase of Kr-X bond (from F to I)
10 the opposite Kr-O bond was increased. Kr-X bond length was increased from FKrOH to IKrOH, but the increment value for IKrOH and BrKrOH was less than that of for ClKrOH.

Table 1 Optimized structural parameters for XKrOH, as obtained from CCSD/AUG-CC-PVTZ calculations, and transition states of the
15 decomposition reactions, as obtained from MP2/AUG-CC-PVTZ. Bond lengths (R) are in Å and bond angles (A) and dihedral angles (D) are in degrees.

Molecule	FKrOH	ClKrOH	BrKrOH	IKrOH
Kr-X	1.919	2.361	2.510	2.740
Kr-O	1.910	1.965	1.997	2.057
O-H	0.963	0.964	0.964	0.967
X-Kr-O	178.2	178.2	179.0	177.9
Kr-O-H	104.5	103.6	103.2	103.0
X-Kr-O-H	177.7	180.0	179.8	179.9
TS1 (for two-body decomposition)				
Kr-X	2.299	2.777	2.912	3.380
Kr-O	1.812	1.831	1.853	1.730
O-H	0.985	0.988	0.988	1.054
X-Kr-O	106.3	105.0	103.2	110.3
Kr-O-H	97.3	96.9	96.3	107.5
X-Kr-O-H	0.0	0.0	0.0	1.7
TS2 (for three-body decomposition)				
Kr-X	3.551	3.450	3.632	3.730
Kr-O	2.849	3.080	3.064	3.060
O-H	0.968	0.968	0.968	0.968
X-Kr-O	178.8	178.7	178.7	178.7
Kr-O-H	106.5	106.5	106.5	106.5
X-Kr-O-H	0.0	0.0	0.0	0.0

Energies and stabilities

20 Because some noble gases are normally unstable, it is important to obtain information about their reactivities, relative stabilities and kinetic properties of their decompositions. For this purpose, we first studied their thermodynamic stabilities as obtained from both formation energies (heats of formation and Gibbs free
25 energies of formation) and isodesmic reactions.[56,57]

Both formation energies and relative stabilities were important data for new structures. The heats of formation and Gibbs free energies of formation, which were calculated by four methods (CCSD, CCSD(T), B3LYP and CAM-B3LYP) with AUG-CC-
30 PVTZ basis set using atomization energy method,[55] were calculated. The results are listed in Table S1 (to save space). The heats of formations calculated by CCSD, CCSD(T), CAM-

B3LYP and WB97XD for FKrOH to BrKrOH were between
39.4-66.3 kcal/mol, 20.9-45.5 kcal/mol, 22.6-56.0 kcal/mol and
35 25.7-57.6 kcal/mol, respectively. The positive values of formation energies showed that these molecules had not been prepared automatically, but their values were not high enough to be synthesized. Based on the nature of these methods, it seems that the CCSD(T) methods could give more valuable data. For
40 both ΔH^o_f and ΔG^o_f, the order of formation energies was found to be as follows: FKrOH<ClKrOH<BrKrOH<IKrOH. The formation energies of ClKrOH and BrKrOh were close to each other. It should be noticed that because these molecules were not isomers, a direct comparison between these values was not so
45 reliable. Based on these data, FKrOH could be prepared more easily than ClKrOH and BrKrOH. In addition, the preparation of IKrOH was the most difficult among these molecules.

Table 2 Relative stabilities of XKrOH compounds (in kcal/mol) as obtained from the isodesmic reaction ($KrX_2 + 2 FKrOH \rightarrow KrF_2 + 2$
50 XKrOH)

X in XKrOH	CAM-B3LYP 6-311++G**	CAM-B3LYP Aug-CC-VTZ	WB97XD 6-311++G**	WB97XD Aug-CC-VTZ	MP2 6-311++G**	MP2 Aug-CC-VTZ	CCSD 6-311++G**	CCSD Aug-CC-VTZ	CCSD(T)[b] Aug-CC-VTZ
F	0	0	0	0	0	0	0	0	0
Cl	2.8	2.5	2.6	2.3	1.9	1.4	2.9	2.4	13.0
Br	4.3	4.2	4.0	3.9	2.4	2.3	4.2	4.1	14.5
I	6.5	5.3	6.3	5.0	--[a]	0.2	--[a]	4.7	17.3

[a] no valuable data were obtained for these cases
[b] The single point energies were obtained from the CCSD(T) calculations and used to correct the results of CCSD calculations

55 To have more sophisticated insights into the relative stability of these structures (non-isomer compounds), we employed the isodesmic reaction. This is a reaction in which the type of chemical bonds broken in the reactant is the same as the type of bonds formed in the reaction product.[56,57] This type of reaction is
60 often used as a hypothetical reaction in thermochemistry. We used equation 5 as an isodesmic reaction to calculate the relative stabilities of molecules (versus FKrOH). The results are listed in Table 2.

$KrX_2 + 2 FKrOH \rightarrow KrF_2 + 2 XKrOH$ (Eq. 5)

65 In this reaction, in the left side, two Kr-F and two Kr-X (X is Cl, Br and I) bonds are broken and the same bonds are formed in the right side of the reaction. The enthalpy of this reaction for each halogen (other than F) showed the relative stability of the produced molecule toward FKrOH. From our calculations and in
70 all levels of calculations, the relative stabilities of XKrOH molecules can be as follows: FKrOH>ClKrOH>BrKrOH >IKrOH. These results confirmed previous data based on formation energies (reported in Table S1) and the relative stabilities of these molecules in all levels of theory were similar
75 to the relative formation energies. Therefore, from F to I, the stability of XKrOH molecules was decreased probably because

the efficiency and power of X-Kr bond were decreased.

Table 3 The kinetics and thermodynamics of decomposition reactions of XKrOH at two levels of theory (MP2/AUG-CC-PVTZ and CAM-B3LYP/AUG-CC-PVTZ). All energy values are reported in kcal/mol and the rate constants are reported in Sec⁻¹

XKrOH → Kr + HOX					
CAM-B3LYP	ΔG	$\Delta G^{\#}$	K_{eq}	k	Barrier (E+ZPE)
FKrOH	-50.68	51.22	1.41E+37	1.76E-25	52.10
ClKrOH	-74.88	42.81	7.76E+54	2.60E-19	43.79
BrKrOH	-78.08	40.54	1.72E+57	1.19E-17	41.67
IKrOH	-84.69	57.06	1.19E+62	9.28E-30	57.66
CCSD(T)/AUG-CC-PVTZ //MP2/AUG-CC-PVTZ					
FKrOH	-49.02	76.16	8.52E+35	9.22E-44	76.86
ClKrOH	-70.19	70.03	2.80E+51	2.90E-39	70.52
BrKrOH	-72.63	65.23	1.74E+53	9.49E-36	65.51
IKrOH	-86.93	34.74	5.27E+63	2.11E-13	33.68
XKrOH→Kr + X + OH					
CAM-B3LYP	ΔG	$\Delta G^{\#}$	K_{eq}	k	
FKrOH	-10.32	90.57	3.68E+07	2.52E-54	92.36
ClKrOH	-29.82	58.62	7.25E+21	6.65E-31	60.10
BrKrOH	-35.16	50.77	5.96E+25	3.79E-25	52.07
IKrOH	-42.33	38.77	1.07E+31	2.38E-16	39.55
CCSD(T)/AUG-CC-PVTZ //MP2/AUG-CC-PVTZ					
FKrOH	-9.78	56.31	1.48E+07	3.28E-29	57.63
ClKrOH	-24.32	35.94	6.73E+17	2.83E-14	36.85
BrKrOH	-26.90	34.58	5.20E+19	2.80E-13	35.14
IKrOH	-26.04	27.56	1.23E+19	3.88E-08	29.89

In addition to thermodynamic stabilities, it is important to study the kinetic stabilities of new compounds (especially for rare gas molecules) to investigate their decomposition reactions. Based on the previous reports, two-body (XKrOH→Kr+HOX) and three-body (XKrOH→Kr+H+OX) mechanisms were possible routes for the decomposition of these molecules. Therefore, we examined both decomposition routes to evaluate thermodynamic and kinetic stabilities of XKrOH molecules. The energy profiles for both routes were calculated carefully and the appropriate transition states were found and approved using suitable methods (as described in the method section). For both ways, the energy results are arranged in Table 3, and the optimized structures of TS (transition states) are shown in Fig. 1. Molecular parameters of these transition states are listed in Table 1 too.

In the two-body decomposition route, XKrOH was decomposed to Kr and HOX. A four-membered ring was obtained as a structure of TS1 (transition states for the two-body decomposition). Each transition state had a planar structure and the values of Kr-O bond lengths and X- Kr-O angles were decreased (versus the parent structures) to provide the possibility of the four-membered ring. However, O-H bond lengths and Kr-O-H angles were not changed meaningfully. In Table 3, Gibbs free energy differences between reactant and products (ΔG),

energy barriers ($\Delta G^{\#}$), equilibrium constants (Keq), rate constants (k) and barrier energies (E+ZPE) for both decomposition routes have been calculated at CCSD(T)/AUG-CC-PVTZ//MP2/AUG-CC-PVTZ (MP2/AUG-CC-PVTZ optimization and frequency calculations followed and corrected by CCSD(T)/AUG-CC-PVTZ single point calculations) and CAM-B3LYP/AUG-CC-PVTZ levels of theory. The decomposition Gibbs free energies in CAM-B3LYP calculations were between -50.68 to -84.69 kcal/mol and in CCSD(T)/MP2 calculations, between -49.02 to -86.93 kcal/mol. Therefore, by considering large values for all equilibrium constants, we can say that the products of decomposition were more stable than XKrOH. These data has been supported previously from the heats of formations. Moreover, the increase in the value of equilibrium constant from FKrOH to IKrOH was observed, thereby showing that the thermodynamic stability of these molecules was decreased from F to I. According to our previous work on xenon, this order can be attributed to more electronegativity of fluorine versus iodine, because by increasing the electronegativity of halogen atoms connected to krypton, the krypton electron pairs were absorbed more powerfully and the electronic repulsions were decreased. However, contrary to this low thermodynamic stability of XKrOH, they had good kinetic stabilities at room temperature because all rate constants were small. The values of energy barriers (by Gibbs free energy) for FKrOH, ClKrOH, BrKrOH and IKrOH were, respectively, 51.22, 42.81, 40.54 and 57.06 kcal/mol by CAM-B3LYP calculations and 76.16, 70.03, 65.23 and 34.74 kcal/mol by CCSD(T)/MP2 calculations. This means that decompositions would be easier from FKrOH and IKrOH. Overall, all decomposition rates were small (less than 2.11E-13) and these compounds had good kinetic stabilities in this decomposition way.

In the three-body decomposition way (route 2 via TS2), ΔG values were remarkably larger than those in route 1 and this route was less favorable than route 1 (by thermodynamic data). However, the same order with route 1 was observed for different molecules. From FKrOH to IKrOH, the ΔG of the decomposition tended to more negative values. The decomposition Gibbs free energies for route 2 in CAM-B3LYP calculations were between -10.32 to -42.33 kcal/mol and in CCSD(T)/MP2 calculations, between -9.78 to -26.04 kcal/mol. However, the kinetic data obtained from the two methods were meaningfully different. The values of energy barriers (by Gibbs free energy) for FKrOH, ClKrOH, BrKrOH and IKrOH were, respectively, 90.57, 58.62, 50.77 and 38.77 kcal/mol in CAM-B3LYP calculations (higher barriers than route 1) and 56.31, 35.94, 34.58 and 27.56 kcal/mol in CCSD(T)/MP2 calculations (smaller barriers than route 1). This means that by the kinetic data, the route 2 was more favourable than route 1 and from FKrOH to IKrOH, the barrier energy for the three-body decomposition was decreased. Therefore, by the second route, in addition to thermodynamic stabilities, the kinetic stabilities of XKrOH molecules were reduced from F to I. By considering all rate constants in both routes, all decompositions had high barrier energies and it could be said that all other molecules had high kinetic stabilities.

Frequencies

Table 4 presents the calculated harmonic vibrational frequencies, force constants and IR intensities for XKrOH structures at the

MP2, CAM-B3LYP and CCSD levels of theory. As shown, at the CCSD/Aug-CC-PVTZ calculations (the highest level of theory), the harmonic X-Kr stretching frequencies for X=F, Cl, Br and I were 448, 292, 208 and 156 cm-1, respectively, the same as

[5] orders found in other levels. Obviously, F-Kr bond had the strongest modes (because it was the strongest bond) and the value of X-Kr stretching mode, its intensity and relative force constant was decreased from F to I. X-Kr bond had the least IR intensity and force constant compared to other stretching modes (Kr-O and

[10] O-H). The O-H frequency values were in the range of 3606-3664 cm^{-1} and this bond had nearly the same frequency among all XKrOH molecules. Surely, if we consider the role of hydrogen bonding in this bond, the OH frequency can be decreased. In addition, the intensities of OH harmonic vibrations (between 91

[15] and 158) were higher than X-Kr and all bending modes, but not more than Kr-O stretching mode. The Kr-O Stretching frequencies had the most intensity among all vibrational modes.

This bond showed ordered values, with frequency being decreased from FKrOH to IKrOH, the same as X-Kr order. It can

[20] be proposed that by the increase of helogen's electronegativity in XKrOH, the halogen atom attracted krypton nonbonding electrons, reduced the electron repulsion between Kr and O and increased the strength of Kr-O bond more efficiently.

Another part of the vibrational mode consisted of bending

[25] vibrations. All bending vibrations had smaller frequencies, intensities and force constants compared to stretching vibrations. Two in-plane and out-of-plane modes for X-Kr-O bending vibrations were close to each other and both of them had less frequencies and intensities than those of Kr-O-H bending. The

[30] bending modes for X-Kr-O bond were in the range of 17-232 cm^{-1} and its angle was around 180 degrees while the bending of Kr-O-H (their angles were around 103 degrees) was harder and their values were between 747 to 1066 cm^{-1}.

[35] **Table 4** MP2, CAM-B3LYP, and CCSD harmonic vibrational frequencies (in cm^{-1}), IR intensities (the first value in parentheses) and force constants (the second value in parentheses) of XKrOH

CAM-B3LYP/Aug-CC-PVTZ	FKrOH	ClKrOH	BrKrOH	IKrOH
in plane bending X-Kr-o	226 (11,0.3)	170 (5,0.2)	150 (3,0.1)	131 (3,0.1)
out of plane bending X-Kr-o	232 (10,0.5)	175 (4,0.3)	155 (2,0.1)	135 (1,0.1)
bending Kr-O-H	1066 (38,0.8)	999 (27,0.7)	968 (24,0.6)	894 (21,0.6)
Stretching X-Kr	471 (53,2.3)	297 (47,1.8)	213 (21,1.3)	174 (7,0.8)
Stretching Kr-O	560 (268,3)	477 (251,1.9)	447 (264,1.6)	409 (289,1.3)
Stretching O-H	3657 (107,9.1)	3659 (145,9.1)	3654 (157,9.1)	3663 (150,9.1)
MP2/Aug-CC-PVTZ				
in plane bending X-Kr-o	205 (10,0.3)	127 (5,0.1)	87 (5,0)	17 (4,0)
out of plane bending X-Kr-o	217 (8,0.4)	143 (3,0.2)	110 (1,0.1)	72 (0,0)
bending Kr-O-H	984 (35,0.7)	898 (37,0.6)	854 (43,0.5)	747 (34,0.4)
Stretching X-Kr	456 (0,2)	301 (0,1.4)	213 (1,0.9)	160 (3,0.5)
Stretching Kr-O	572 (262,4.1)	483 (188,2.6)	460 (119,2.3)	463 (26,2.4)
Stretching O-H	3664 (91,9.3)	3654 (100,9.2)	3652 (97,9.2)	3657 (102,9.3)
CCSD/Aug-CC-PVTZ				
in plane bending X-Kr-o	220 (11,0.3)	154 (5,0.2)	128 (4,0.1)	99 (3,0.1)
out of plane bending X-Kr-o	227 (10,0.5)	159 (3,0.2)	133 (2,0.1)	107 (0,0.1)
bending Kr-O-H	1047 (30,0.8)	977 (21,0.7)	941 (19,0.6)	853 (10,0.5)
Stretching X-Kr	448 (26,2.1)	292 (19,1.5)	208 (7,1)	156 (3,0.6)
Stretching Kr-O	543 (295,3.3)	461 (242,2.1)	433 (205,1.8)	421 (119,1.6)
Stretching O-H	3615 (95,9.3)	3608 (125,9.2)	3606 (132,9.2)	3611 (113,9.3)

NBO analyses

Atomic charges, atomic hybridizations (Table S2) and the interactions between different orbitals (second-order perturbation

[40] energies, Table 5) were important molecular properties that could be obtained from NBO calculation. In these tables, for the sake of brevity, the results of NBO calculations were collected using CCSD/AUG-CC-PVTZ level of theory to determine atomic and interatomic properties. NBO atomic charges listed in the first part

[45] of Table S2 showed that the maximum negative charges were placed on oxygen and then, halogens.

The maximum positive charges were placed on krypton and then, hydrogen in all molecules. Because krypton was linked to two electronegative atoms, it had a greater positive charge than

[50] hydrogen. Moreover, the negative charges of oxygen were decreased for FKrOH and ClKrOH and increased for BrKrOH and IKrOH and the positive charges for both krypton and hydrogen were decreased from FKrOH to IKrOH because of decreasing halogen's electronegativity. It should be noted that the

[55] net charge placed on krypton was between 0.654-1.069, from FKrOH to IKrOH, thereby showing that by the increase of net charge on krypton, the stability of the molecule (according to

Table 2) was increased. In other words, krypton tended to make bonds with other atoms when other atoms had the highest possible electronegativity to make krypton losses one electron (in the molecule). In this case, the electron configuration around krypton was not octet (that was the reason for atoms to make bond) and it could be incorporated in bonds with another atom.

NBO calculations also consisted of hybridization of Kr, O and H in two Kr-O and O-H bond for FKrOH and ClKrOH and hybridization of Kr, Br, I, O and H in two Kr–I, Kr-Br and O-H bond for IKrOH and BrKrOH. It is noteworthy that no hybridization for Kr-X bond in FKrOH and ClKrOH and Kr-O bond in IKrOH and BrKrOH has been reported, thereby confirming that the nature of Kr-X bond in FKrOH and ClKrOH and Kr-O bond in BrKrOH and IKrOH is ionic and these atoms are connected via electrostatic interactions. In FKrOH and ClKrOH, krypton mostly used its p orbital (97.15% and 97.93%, respectively) in its bond with O and the contribution of its orbital was 1.10% and 0.65%.

Moreover, oxygen, iodine and bromine atoms used p orbital (between 90.95% and 97.38%) in their bonds with krypton while oxygen was nearly hybridized to sp^3 in its bond with hydrogen. This means that Kr-O, Kr-I and Kr-Br were so long bonds that atoms participating in this bond could not use their s orbitals in hybridization with p and the pure p orbitals participated in these bonds.

Table 5 The second order intramolecular perturbation energies obtained from CCSD/Aug-CC-PVTZ calculations

	Donor	Acceptor	E2 (kcal/mol)
FKrOH	F_{LP}	σ^*_{Kr-O}	130.57
	F_{LP}	$Kr_{Rydberg}$	21.88
ClKrOH	Cl_{LP}	σ^*_{Kr-O}	187.19
	Cl_{LP}	$Kr_{Rydberg}$	19.88
BrKrOH	O_{LP}	σ^*_{Kr-Br}	301.12
	O_{LP}	$Kr_{Rydberg}$	26.23
IKrOH	O_{LP}	σ^*_{Kr-I}	224.75
	O_{LP}	$Kr_{Rydberg}$	26.66

The second order perturbation energies, as obtained from NBO calculations, could give us very useful information about interactions via molecules. In this research, we obtained these data using CCSD/AUG-CC-PVTZ calculations. The most important results are listed in Table 5. According to the data listed in the Table 5, for FKrOH and ClKrOH (that we had KrOH$^+$ and X$^-$), a powerful interaction between halogen's lone pair and Kr-O antibonding orbitals (130.57 kcal/mol for FKrOH and 187.19 kcal/mol for ClKrOH) was observed, thereby confirming the strong electrostatic interaction between these two parts. It is important to note that this iteraction in ClKrOH was stronger than that in FKrOH because chlorine orbitals were more similar to krypton orbitals (in size) versus florine. Moreover, a weaker interaction between halogens lone pair and rydberg orbitals of krypton (21.88 kcal/mol for FKrOH and 19.88 kcal/mol for ClKrOH) was observed. Since this interaction is a type of backbonding, it is known that florine has the strongest backbonding and its interaction is more than chlorine interaction.

For BrKrOH and IKrOH (that we have KrBr$^+$, KrI$^+$ and OH$^-$), the oxygen donated its electrons powerfully to Kr-I and Kr-Br antibonding orbital (301.12 kcal/mol for BrKrOH and 224.75 kcal/mol for IKrOH). Another interaction was donating oxygen lone pair to rydberg orbitals of krypton with nearly the same values for both molecules. These data showed that BrKrOH had the biggest interaction among all molecules because bromine was placed in the same row of periodic table with krypton and their orbitals (both having 5p orbitals) had the most strong interactions. After BrKrOH, IKrOH had strong interactions because of the large polarizability of iodine atom.

QTAIM analysis

From the QTAIM Analyses, the ρ (electronic density), the Laplacian of ρ and ε values (π bond character) were calculated for three existing bonds in this molecule, Kr-O, Kr-X and O-H (Table S3). Among these three bonds, O-H bonds had the maximum value of ρ and Kr-X bonds had the minimum value of ρ. The electron density had a direct relation with the bond strength and an inverse relation with the bond length. This was the reason for this order. The values of ρ were in the range of 0.141-0.066 au for Kr-O bonds and 0.372-0.359 au for O-H bonds. These values were decreased from FKrOH to BrKrOH and then increased from BrKrOH to IKrOH. However, the ρ values of Kr-X bonds (in the range of 0.085-0.037 au) were decreased from FKrOH to IKrOH by decreasing the electronegativity of halogen atoms. The Laplacian of ρ ($\blacktriangledown^2\rho$) at critical points showed the charge concentration between the two atoms in the bonds. These values were positive for Kr-O and Kr-X bonds and negative for O-H bonds. The sign of $\blacktriangledown^2\rho$ showed that both Kr-X and Kr-O bonds had an electrostatic nature (closed shell) and OH bond had a covalent nature (electron sharing). By looking at QTAIM data, we could see that these values followed the same order as that of ρ, thereby explaining that by the increase of ρ, the absolute value of $\blacktriangledown^2\rho$ was increased and clearly, both ρ and $\blacktriangledown^2\rho$ obeyed similar rules. For better presentation of these values, the contour plots of ρ and $\blacktriangledown^2\rho$ have been depicted in Fig. 2. The distorted shapes of electron density on Kr confirmed the charge transfer between them and other atoms. In addition, both O and X had distorted charge concentration (in$\blacktriangledown^2\rho$ plots) toward krypton. The $\blacktriangledown^2\rho$ plots also showed the unique structure for O-H bond, confirming its covalent nature. Also, the separated lines for Kr-X and Kr-O bonds proved their electrostatic interactions.

Another parameter, ellipticity (ε), could provide structural insight as an indicator of π character and also, indicate delocalization through hiperconjugation. According to the data in Table S3, the Kr-O bonds had the maximum value of ε and the Kr-X bond had the minimum value of ε among all three bonds of each molecule. Therefore, consistent with the previous data, the Kr-O bond was very strong even in IKrOH. Since the halogen atoms generally interacted with the adjacent atoms by back-bonding, they attracted the electron pairs of oxygen and caused the strength for the Kr-O bond. Furthermore, the ε values for Kr-X bond in all molecules were very small (between 0.001 and 0.050) because of the long bond length between Kr and halogen. In general, it can be suggested that the Kr-X bond can be easily broken.

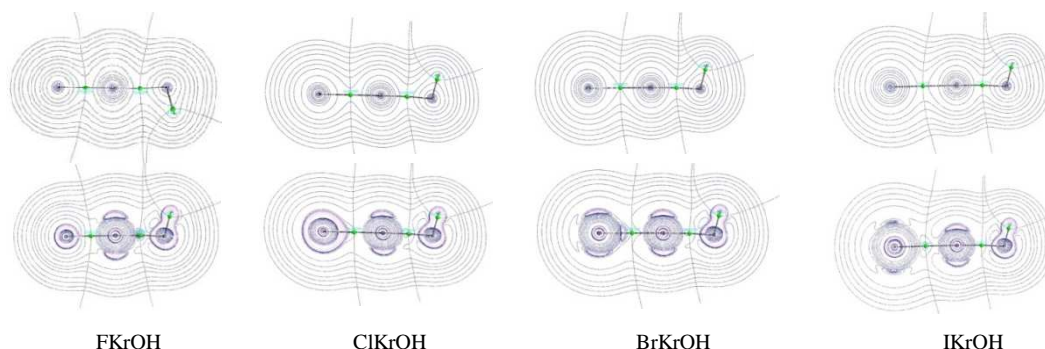**ARTICLE TYPE**

| FKrOH | ClKrOH | BrKrOH | IKrOH |

Fig. 2 Contour plots of ρ (top) and Laplacian of ρ (bottom) for all XKrOH obtained from population analyses at CCSD/Aug-CC-PVTZ level of theory
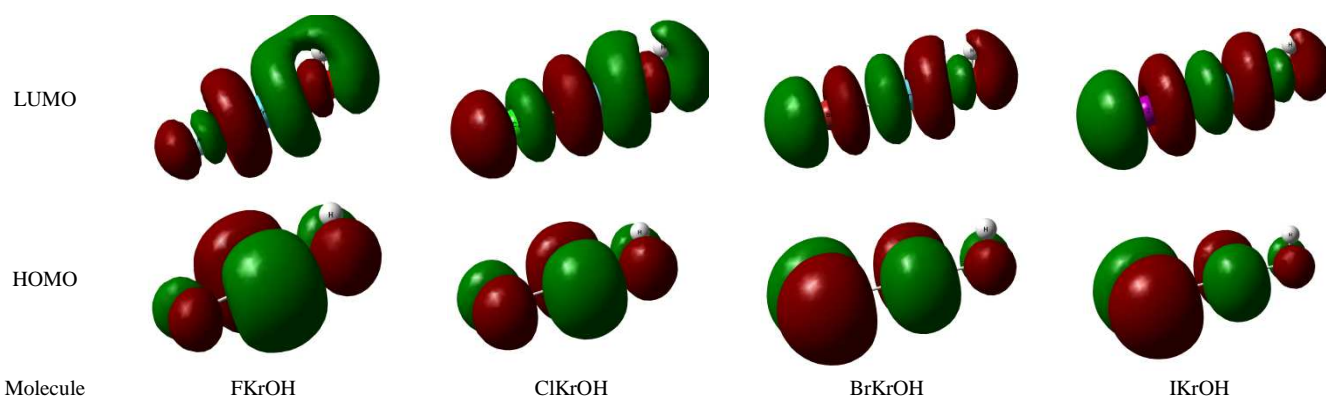

LUMO				
HOMO				
Molecule	FKrOH	ClKrOH	BrKrOH	IKrOH

Fig. 3 The graphical presentation of HOMO and LUMO for all molecules at CCSD/Aug-CC-PVTZ level of theory

Population analysis

The shapes and energies of HOMO and LUMO of all molecules, as obtained from the population calculations, are shown in Fig. 3. In HOMO orbitals, from FKrOH to IKrOH, the electron density of halogen was increased and the electron density of krypton and OH group was decreased, especially for BrKrOH and IKrOH. In other words, from FKrOH to IKrOH, the density of negative charge was displaced from the OH side of the molecule to X, in accordance with the previous data. Meanwhile, the energy of HOMO and the energy gap between HOMO and LUMO (listed in Table S4) were decreased from FKrOH to IKrOH. Thus, IKrOH had the least energy gap and FKrOH had the most energy gap, causing the higher reactivity of this molecule. Also, the rate constants of this molecule were in accordance with these results, as shown previously in Table 3. From the energies of HOMO and LUMO, which were obtained from population analysis, some useful reactivity parameters such as chemical potential (μ), chemical hardness (η), global softness (S) and electrophilicity index (ω) were calculated as defined in equations 1-4 (section 2). Chemical potential is a criterion of reactivity. IKrOH had the highest chemical potential; therefore, it was the most reactive molecule among these structures (also, the least stable). The chemical hardness of molecules was decreased from FKrOH to IKrOH by increasing the size of halogen atom (according to our expectation) and the reverse order could be observed for global

softness. Finally, the electrophilicity indexes were increased from FKrOH to IKrOH, showing that IKrOH was the most appropriate molecule for nucleophilic attack.

Conclusions

In this report, optimized geometries, molecular properties, vibrational frequencies, NBO atomic charges and hybridizations of XKrOH (X = F, Cl, Br and I) molecules at their equilibrium geometries were investigated using CCSD, CCSD(T), MP2, CAM-B3LYP and WB97XD methods and large basis sets. Among these molecules, IKrOH and BrKrOH molecules showed two I- , Br - and KrOH+ parts, while in other molecules, they could be presented as XKr+ and OH-. A decomposition route was proposed for these molecules, showing high exothermic reactions especially for the two-body decomposition. However, despite their low thermodynamic stabilities, their decomposition rate constants were small and all molecules, except IKrOH in the three-body decomposition, had high kinetic stabilities. These data indicated the possibility for the identification and characterization of these molecules. In addition to the calculation of their vibrational frequencies, NBO atomic charges and hybridizations, to calculate electron densities, bond elipticities and laplacian of electron densities, the bonding properties of XKrOH molecules were studied by AIM calculations; also, for second order intramolecular perturbation energies, NBO calculations were

used. Moreover, by using heats of formations, Gibbs free energies of formations and isodesmic reactions, the relative stabilities of XKrOH molecules were studied. These calculations showed that the stability of XKrOH molecules was decreased from F to I, in accordance with other bonding and energy properties. Finally, reactivity parameters, as obtained from population analysis, confirmed the increase in reactivity and the decrease in stability form FKrOH to IKrOH.

Notes and references

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Table of content:

A theoretical study of stabilities, reactivities and bonding properties of XKrOH (X= F, Cl, Br and I) as potential new krypton compounds using coupled cluster, MP2 and DFT calculations

Hossein Tavakol,* Fahimeh Hassani and Akram Mollaei-Renani

DFT and Ab initio calculations were employed to disclose the conceivable existence of new noble gas molecules, XKrOH.