

Electronic structure and thermodynamic properties of YIrC and YIrC₂

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Abstract

Ab initio calculations including Møller–Plesset second order perturbation (MP2), density functional theory (DFT), complete active space self-consistent field (CASSCF) and multireference singles and doubles configuration interaction (MRSDCI) computations are carried out for the YIrC and YC₂Ir molecules. Several alternative structures are optimized and the vibrational frequencies are computed. Thermodynamic properties such as the Gibbs energy functions and heat content functions are computed and compared with the available experimental data. The nature of chemical bonding in these molecules is analyzed.

1. Introduction

Transition metal carbides are of wide interest as they find numerous applications in several areas ranging from surface chemistry to astrochemistry. Recent developments in the chemistry of metal–carbon clusters and metallo-fullerenes have stimulated many studies on such systems [1]. Although gaseous transition metal carbides have been observed first in 1958 [2], there is little insight available into the nature of the metal–carbon bonding [3]. Gaseous metal carbides have been the subjects of several experimental studies [4], [5], but theoretical investigations have been restricted to very few small clusters [6], [7].

Thermodynamic data such as the Gibbs free energy and the enthalpies of formation have been obtained by the Knudsen effusion mass spectrometry [8], [9]. Most of the experimental studies have been focused on rare earth carbides and mixed metal rare earth carbides [4], although carbides containing two different metals have also been detected [4]. Mixed yttrium iridium carbides such as YIrC and YIrC₂ have been identified by Pelino et al. [10] using the Knudsen effusion mass spectrometry. The enthalpies of formation were measured using the third law method. From these values Pelino et al., have deduced the atomization energies of these species. The third law treatment of the thermodynamic data requires some knowledge of the structures and vibrational frequencies of these species. As noted by these authors, the structures of these molecules are not known, and thus these authors have estimated the molecular properties of these species based on analogy with rare earth carbides. However, our current

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theoretical study shows that the geometries assumed by Pelino et al., are quite different from our computed geometries.

The objective of this study is to determine the equilibrium structures, vibrational frequencies, atomization energies and thermodynamic properties of YIrC and YIrC₂ molecules using relativistic ab initio techniques including electron correlation effects. We consider several alternative structures and symmetries and perform geometry optimization for each such structure. The nature of the chemical bonding is also considered for these species. The Mulliken population analysis and electron density contours are obtained which provide insight into the nature of bonding in these species. We find that the yttrium atom transfers considerable electronic charge density to Ir which in turn binds to the carbon atoms. The Y atom was not found to be involved in bonding with carbon. Our computed molecular constants facilitate computation of thermodynamic functions such as the Gibbs free energy functions and heat content functions. Our computed results are compared with the experimental data.

2. Theoretical methods and computational details

The geometry searches for different spatial structures of YIrC and YIrC₂ molecules were done at the Møller–Plesset second order perturbation (MP2) [11] level of theory. The geometries of the ground states of these species were also optimized by the complete-active-space-multiconfiguration self-consistent field (CASSCF) [12] and the density functional theory (DFT) [13] methods. The DFT approach utilized the Becke [14] and the Lee–Yang–Parr [15] (correlation) functional. The atomization energies were also calculated within the multireference singles and doubles configuration interaction method including the Davidson correction [16]. The geometry searches were performed by applying the quasi Newton–Raphson procedure [17], [18]. The vibrational frequencies and thermodynamic functions were calculated within the MP2 method by applying ideal gas, rigid rotor and harmonic oscillator approximations [19].

All the calculations described here were made using the relativistic effective core potentials (RE-

CPs) with the 4s²4p⁶4d¹5s² shells included in the valence space for yttrium [20], 5s²5p⁶5d⁷6s² valence shells for iridium [21] and 2s²2p⁶ valence shells for the carbon atoms [22]. The most diffuse exponents in the original basis sets have been left uncontracted leading to (5s4p3d) valence basis sets for Y and Ir and a (3s3p) basis set for C. The carbon basis set was supplemented with a six-component 3d Gaussian functions adopted from Dunning and Hay [23]. The above choice leads to 88 and 106 basis functions for YIrC and YIrC₂, respectively. This basis set was tested earlier and found to be satisfactory for the YC₂ [7] and Ir–CO [24] systems.

The valence orbitals of YIrC comprise 24 orbitals and 36 electrons. Such an internal space is too large for the CASSCF treatment and thus excitations from the lowest 15 orbitals were not allowed, although these orbitals were allowed to relax. The C_s symmetry was used since this allows for the possibility of the molecule to be in a bent geometry. The six active electrons were distributed in the active space of eight a' and three a'' orbitals in all possible ways. The above choice of the active space leads to 4627 configuration spin functions (CSF) for the 'A' electronic state.

The YIrC₂ system was treated in the C_{2v} symmetry. From the complete set of 28 valence orbitals, 13 molecular orbitals were selected to be included in the active space comprising seven a₁, three b₁, four b₂ and one a₂ orbitals in the C_{2v} group. The above active space leads to 6783 CSFs for the 'A₁' electronic ground state.

The MRSDCI method of calculations was employed following the CASSCF technique for the YIrC molecule. All configurations in the CASSCF with coefficients ≥ 0.07 were included as reference configurations in the MRSDCI. The MRSDCI method also correlated the outermost six electrons of the YIrC molecule. All possible single and double excitations were allowed from these reference configurations which resulted in 110,000 CSFs.

The MP2 calculations were performed using the restricted Hartree–Fock method for closed shell systems and the spin unrestricted Hartree–Fock method for the triplet states. The projected values (free from contaminations due to other states) are reported. All electrons not frozen in the RECPs were correlated in this method. The MP2 computations were made

using the Gaussian 94 code [25]. The CASSCF computations were made using the GAMESS [26] program package and also a modified version of ALCHEMY II² to include the RECPs [27]. The MRSDCI computations were made using ALCHEMY II.

3. Molecular structure of YIrC and YIrC₂

At the present time there are no experimental data pertinent to the molecular structures of YIrC and YIrC₂. The structural parameters needed for the evaluation of experimental enthalpies using the third law method were estimated on the basis of known parameters for the analogous rare earth compounds [10].

The most stable structures of YIrC are presented in Table 1. The molecule in the ground state is nonlinear such that the carbon atom is closer to the Ir atom (Fig. 1). The second lowest molecular state is a triplet state at the geometry corresponding to the ground state. The bond lengths adopted in the experimental estimation of the Gibbs free energies are close to the values that we compute for the linear structure.

The YC₂Ir cluster exhibits a kite-like structure in which the Ir atom is closely bonded to the carbon atoms, while the yttrium atom is farther away on the other side exhibiting longer Y–C bonds. The geometry optimization procedure starting from the C_s symmetry leads to the C_{2v} geometry (Fig. 2). The T-shaped C_{2v} structure as well as possible linear structures were also studied (Table 2) but were found to be significantly higher in energy. The above structure is similar to the ground state of YC₂ (nonlinear, symmetrical, and bent structure [7]). Among the linear isomers, the most stable structure corresponds to Y–C–C–Ir. The structural parameters assumed by Pelino et al. [10], in their third law method of estimating the binding energies for the linear structure are reasonably close to our bond lengths in the Y–C–C–Ir linear structure, although this minimum

Table 1

The calculated geometries and energy separations, ΔE for YIrC

Species	Electronic state		MP2	DFT	CASSCF	Other ^a
YIrC bent	¹ A'	R(C–Y)	2.45	2.55	2.57	2.06
		R(C–Ir)	1.73	1.76	1.70	1.683
		R(Y–Ir)	2.55	2.53	2.83	2.481
	³ A'	\angle YCIr	72.8	72.9	80.4	146°
		ΔE	0.0			
		R(C–Y)	2.55			
Y–Ir–C linear	¹ Σ^+	R(C–Ir)	1.67			1.683
		R(Ir–Y)	2.68			2.481
		ΔE	4.49			
	³ Σ^+	R(C–Ir)	1.53			
		R(Ir–Y)	3.17			
		ΔE	4.13			
Ir–Y–C linear	¹ Σ^+	R(C–Y)	1.94			2.06
		R(Ir–Y)	2.71			2.481
		ΔE	9.22			
Y–C–Ir linear	¹ Σ^+	R(C–Y)	2.26			2.06
		R(C–Ir)	1.67			1.683
		ΔE	7.21			

Distances are in Angstrom, angles in degrees and energy separations in eV.

^a Molecular parameters used in the evaluation of experimental thermodynamic functions Ref. [10].

is not the ground state of the YC₂Ir molecule (see Table 2).

4. The nature of the chemical bonds in yttrium–iridium carbides

The nature of bonding in transition metal carbides can be understood through the Mulliken population analysis. Table 3 shows the atomic charges and atomic orbital populations of the ground states of YIrC and YC₂Ir as derived from their Mulliken populations. As seen from Table 3, the populations are significantly different for the two molecules considered here. In the case of YIrC, there is considerable charge transfer from Y to Ir. The Ir atom transfers most of the electron density it receives from

² The major authors of ALCHEMY II are B. Lengsfeld, B. Lui and M. Yoshimine.

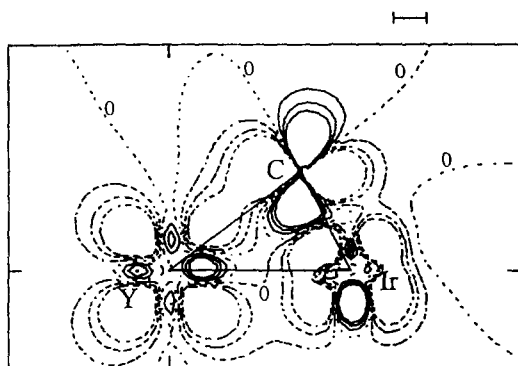


Fig. 1. The electron density difference maps between YClr, and Y, C and Ir atoms in the YClr molecular plane. The maps were derived from the CASSCF natural orbitals. The spacing between the contours is 0.01 electron/bohr³. The contours with no density change are labelled with zeros, while solid lines indicate enhancement of electronic density.

Y to the carbon atom. The net result is that Ir gains only slight electronic density.

In the case of YC₂Ir, the Y atom transfers about one electron to the carbon atoms, while the Ir atom becomes electron rich through some net charge transfer from the carbon atoms. The above picture is consistent with the chemical bond in Y–C [6] for which the Mulliken population analysis indicates a transfer of 0.7 electron.

In both molecules considered here, the bonds are formed according to a general model of σ donation (from the s and d atomic orbitals of the metal atom)

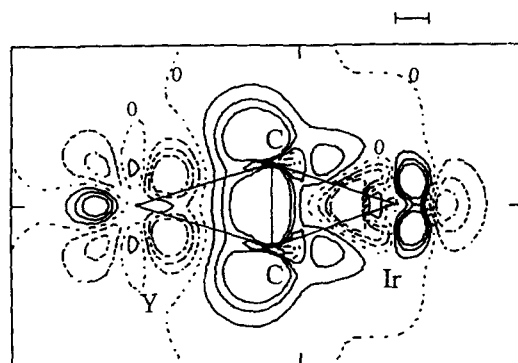


Fig. 2. The electron density difference maps between YC₂Ir and the dissociated Y, C₂, and Ir fragments. The maps were derived from the CASSCF natural orbitals. Technical data are the same as for Fig. 1.

Table 2

The calculated geometries and energy separations, ΔE for YIrC₂

Species	Electronic state	MP2	DFT	CASSCF	Other ^a
YC ₂ Ir kite, C _{2v}	¹ A ₁	R(C–C)	1.44	1.42	1.34
		R(Y–C)	2.16	2.19	2.20
		R(Ir–C)	1.88	1.90	2.02
		ΔE	0	0	0
	³ A ₁	R(C–C)	1.38		
		R(Y–C)	2.20		
		R(Ir–C)	1.91		
		ΔE	1.57		
Y–C–C–Ir linear	¹ Σ^+	R(C–C)	1.34		1.27
		R(Y–C)	2.02		1.82
		R(Ir–C)	1.71		1.75
		ΔE	1.85		
	³ Σ^+	R(C–C)	1.32		
		R(Y–C)	2.07		
		R(Ir–C)	1.73		
		ΔE	1.98		
Ir–Y–C–C linear	¹ Σ^+	R(C–C)	1.29		1.27
		R(Y–C)	2.14		1.72
		R(Ir–Y)	2.75		2.481
		ΔE	4.89		
Y–Ir–C–C linear	¹ Σ^+	R(C–C)	1.32		
		R(Ir–C)	1.89		
		R(Y–Ir)	2.13		
		ΔE	2.24		
Y–Ir–C ₂ T-shape, C _{2v}	¹ A ₁	R(C–C)	1.66		
		R(Ir–C)	1.79		
		R(Y–Ir)	2.70		
		ΔE	2.04		
Ir–Y–C ₂ T-shape, C _{2v}	¹ A ₁	R(C–C)	1.28		
		R(Y–C)	2.25		
		R(Ir–Y)	2.73		
		ΔE	3.48		

Distances are in Angstrom, angles in degree and energy separation in eV.

^a Molecular parameters used in the evaluation of experimental thermodynamic functions Ref. [10].

and π back donation (p atomic orbitals) from the carbon atom(s) to the metal (Table 3). The dipole moment is significantly larger for the YC₂Ir molecule, in agreement with the larger charge separation. The description of bonding is qualitatively similar for the MP2 and CASSCF methods, although the dipole moments are significantly underestimated in the CASSCF method due to inclusion of electron correlation effects to a smaller extent.

Table 3

The atomic charges, atomic orbital populations (from Mulliken analysis) and dipole moments (in Debye) for ground state structures of YIrC and YC₂Ir

Atom		YIrC		YC ₂ Ir	
		MP2	CASSCF	MP2	CASSCF
Y ^a	charge	0.468	0.492	1.013	1.155
	s	3.471	3.567	3.086	2.888
	p	6.210	6.286	6.190	6.350
	d	0.851	0.654	0.710	0.607
Ir ^a	charge	−0.107	−0.068	0.175	0.069
	s	4.022	4.342	3.824	3.702
	p	6.107	6.071	6.138	6.162
	d	6.978	6.654	6.863	7.058
C ^b	charge	−0.361	−0.424	−0.594	−0.612
	s	1.850	1.828	1.621	1.589
	p	2.422	2.495	2.853	2.907
	d	0.089	0.101	0.118	0.115
Dipole moment		2.508	1.519	3.989	2.140

^a The populations of Y and Ir atoms include the semicore $(n-1)s^2(n-1)p^6$ shells.

^b In case of YC₂Ir, the C atoms are equivalent and thus the listed populations are per carbon atom.

The differences in the electronic distribution can be visualized by the electron density difference maps shown in Figs. 1 and 2 for YIrC and YC₂Ir, respectively. In both cases, as seen from these figures, the Y atom loses electron density while the Ir and carbon atoms gain electron density. The π back donation from the C₂ fragment to the Ir atom is also

Table 4

The atomization enthalpies ($\Delta H_{a,0}^\circ$) for the ground states of YIrC and YC₂Ir (in kJ/mol)

Method	YIrC	YC ₂ Ir
MP2	1221	1644
MP2(ZPV) ^a	1211	1631
DFT	1046	1477
CASSCF	916	
MRSDCI	939	
Expert ^b	984–1023	1660–1700

^a Includes zero-point correction.

^b Ref. [10].

clear from Fig. 2. In both cases there is considerable covalent bonding between Ir and C atoms made possible through the donation of electronic charge from the metal atom and back donation from the carbon to the Ir atom.

5. Thermodynamic properties of YIrC and YC₂Ir

The experimental atomization energies have been evaluated from the third law method using assumed geometries for YIrC and YC₂Ir [10]. Table 4 shows our computed thermodynamic functions for different temperatures together with the experimental data from Ref. [10]. Our computed results are derived from the MP2 equilibrium geometries, vibrational frequencies, and partition functions. The experimental values were derived in Ref. [10] based on assumed geometries. The agreement between our theo-

Table 5

Gibbs energy functions, $GEF = (G_T^\circ - H_0^\circ)/T$, and heat content functions, $\Delta H = H_T^\circ - H_0^\circ$ for YIrC and YC₂Ir

Molecule	Method		Temperature (K)						
			298	2000	2200	2400	2600	2800	3000
YIrC	MP2	GEF	−264.2	−355.9	−361.0	−365.7	−370.1	−374.2	−378.0
		ΔH	12.3	107.6	119.2	130.8	142.4	154.0	165.6
	Est ^a	GEF	−275.3	−364.4	−369.4	−374.1	−378.4	−382.4	−386.2
		ΔH	12.0	105.7	117.2	128.7	140.3	151.9	163.2
	MP2	GEF	−266.4	−369.4	−375.8	−381.7	−387.2	−392.3	−397.1
		ΔH	12.3	132.9	148.2	163.6	179.1	194.8	210.5
YC ₂ Ir	Est ^b	GEF	−266.6	−381.3	−388.4	−395.0	−401.1	−406.8	−412.2
		ΔH	13.4	148.3	165.4	182.6	199.8	217.0	234.3

^a Y–C–Ir bent, from Ref. [10].

^b Y–C₂–Ir linear, from Ref. [10].

retically computed thermodynamic functions and the experimental results is quite good, in spite of the incorrect geometries used in the experimental estimation. However, due to a multiconfigurational nature of the wave function near the equilibrium geometry and the dissociation limits, the MP2 method overestimates the atomization energies. The multiconfigurational CASSCF/MRDCI calculations for YC₂Ir molecule yielded lower atomization energy. The C² for the main configuration of the equilibrium geometry of YC₂Ir(12a⁽²⁾, 4a^{u(2)}) was found to be near 0.8, consistent with a multi-configurational nature of the wave function.

The differences between the electronic energies for different molecular structures are quite significant in the computation of the atomization energies. However, the thermodynamic functions such as the Gibbs free energy and heat content functions are less sensitive to the structural parameters. Our calculated Gibbs energy functions (GEF) and heat content functions are close to the estimated experimental values in Ref. [10] (Table 5).

The experimental atomization energies may be corrected via the relation

$$\Delta = -T(\text{GEF}_{\text{est}} - \text{GEF}_{\text{MP2}}).$$

The corrections thus computed for the atomization energies are 17–24 kcal/mol for YC₂Ir and 24–45 kcal/mol for YC₂Ir depending on the temperatures used in the computations. These values lie within the error bars of the experimental measurements.

6. Conclusions

The equilibrium geometry of the ground state of YC₂Ir is a very acute triangle in which the Ir atom is closer to the carbon atom compared to the yttrium atom. The other possible structures such as the linear YIrC and YC₂Ir are considerably higher in energy. The YC₂Ir molecule has a kite equilibrium structure with a C_{2v} symmetry. The Ir atom is closer to the two carbons in this structure compared to Y. The linear Y–C–C–Ir isomer and another T-shaped structure are significantly higher in energy.

The nature of chemical bonding in the two species was analyzed through the Mulliken populations and the electron density differences. It was found that the

Y atom donates an electron to the C₂ fragment, which in turn interacts with the Ir atom covalently. The corresponding Y–C bond in YC₂Ir was found to be less ionic since the electronic charge transfer from Y is roughly half of the corresponding value in YC₂Ir. In both cases the bonding is facilitated through metal donation and π back-donation from the carbon to Ir.

The calculated atomization energies agree reasonably well with the experimental values. Although the structure assumed by Pelino et al. [10] for both YIrC and YC₂Ir do not agree with our computed results, the thermodynamic functions such as the Gibbs energy functions are not too sensitive to the geometries. Hence good agreement was found between our computed thermodynamic functions and the experimental results [10].

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