

# Theoretical Study of Structural and Thermodynamic Properties of Yttrium Carbides, $YC_n$ ( $n = 2-6$ )

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Received: November 20, 1995<sup>®</sup>

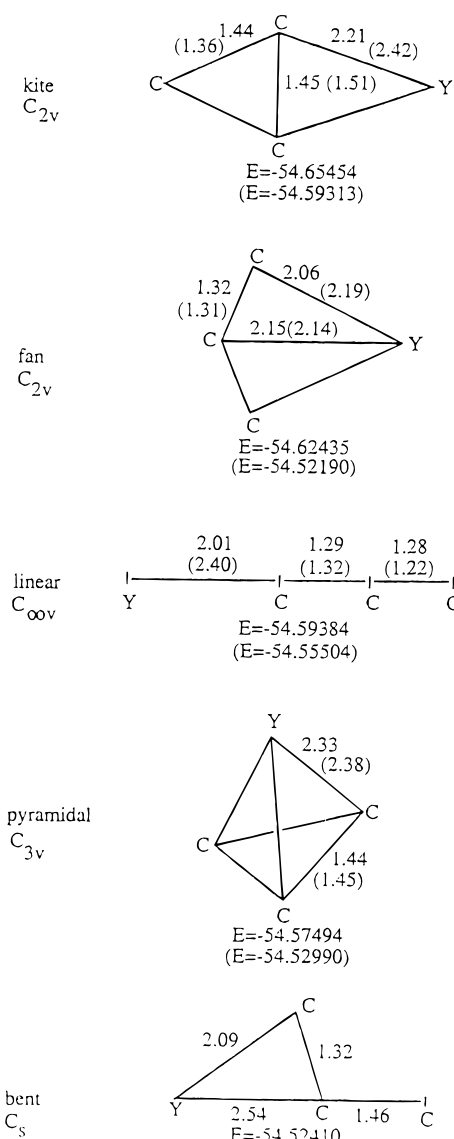
Theoretical studies of monoyttrium carbides,  $YC_n$ , for  $n = 2-6$ , are presented. Consideration of several alternative structures leads to the kite, fan, and linear structures as the most attractive candidates for the ground states of different  $YC_n$  complexes. The Y–C bond is strongly ionic due to the electron transfer from the yttrium to carbon atoms. The computed enthalpies of formation of  $YC_n$ , atomization, and dissociation energies of these species are close to the corresponding experimental data. We compare the thermodynamic properties thus obtained from our theory with the experimentally estimated Gibbs energy functions and heat content functions using assumed structures.

## Introduction

The structures and reactivities of transition-metal carbide clusters are quite important in many areas of chemistry such as surface chemistry, catalysis, combustion chemistry, astrochemistry, solid state chemistry, and so on. Metallofullerenes and metallocarbohedranes,<sup>1,2</sup> which are the subjects of several studies, are examples of metal-carbon systems. These species are generated typically by doping carbon clusters with metal atoms. Metal atoms trapped inside fullerene cages are very stable and have been isolated in macroscopic quantities.<sup>2</sup> The existence of such stable species has stimulated numerous studies on these systems. In spite of such studies, there is very little insight available into the nature of metal-carbon bonding even in small systems.<sup>3</sup>

Transition-metal carbides exhibit high melting points, hardness, and metallic conductivity, which make these materials attractive candidates for several technological applications in electronics and material science. The nature of the transition metal-carbon bonding in these species is rather intriguing, and thus these species are interesting from scientific as well as technological standpoints. Since the first observation of gaseous metal carbides by Chupka et al.,<sup>4</sup> about 20 different metal and mixed-metal carbide systems have been studied.<sup>5,6</sup> Several gas-phase transition-metal carbides and their ions have been studied with the Knudsen effusion mass spectrometry,<sup>7</sup> a technique which readily yields the thermodynamic data. Among the transition-metal carbides, it appears that the yttrium carbides are the most extensively studied, and in particular, experimental results of the thermodynamic stability are available for single-metal carbides  $YC_n$ ,<sup>8-12</sup> dimetal carbides  $Y_2C_n$ ,<sup>13</sup> and YIr carbides.<sup>14</sup> These extensive experimental works have very little support from theoretical studies, and only a few carbides such as Y–C<sup>15</sup> and  $YC_2$ <sup>16</sup> systems have been theoretically studied before.

The gas phase ion/molecule reactions of tantalum carbide clusters,  $TaC_n^+$ , for  $n = 0-14$ , have been studied by Cassady and McElvany.<sup>5</sup> It was shown by these authors that the addition of Ta dramatically alters the reactivity of carbon clusters. In addition, structural isomers were found for  $TaC_7^+$ ,  $TaC_8^+$ , and  $TaC_9^+$ .

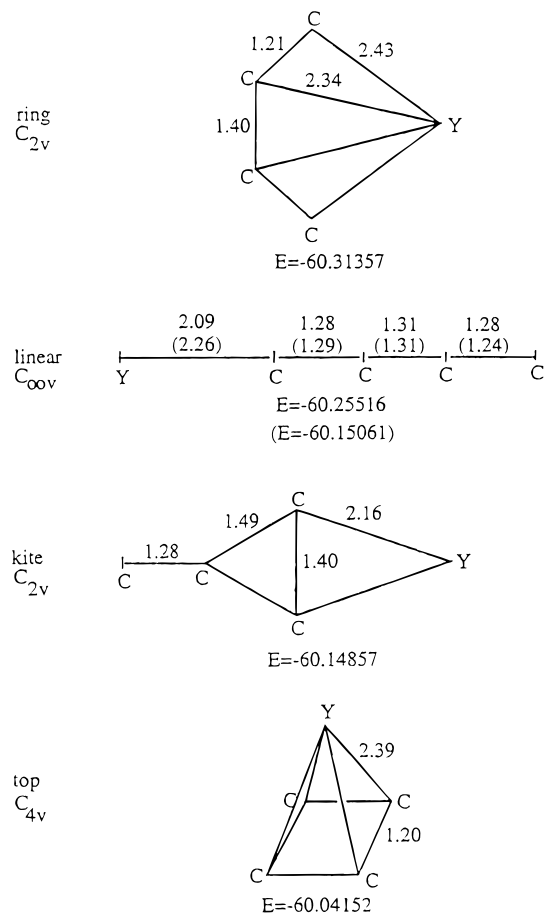


**Figure 1.** Structures and energies ( $E$ ) from MP2 calculations for the doublet and quartet (values in parentheses) electronic states of  $YC_3$ . Distances are in angstroms while energies are in hartrees.

The aim of this work is the determination of molecular structures of  $YC_2$ – $YC_6$ . The atomization energies of  $YC_n$  ( $n$

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, April 15, 1996.



**Figure 2.** Structures and energies ( $E$ ) from MP2 calculations for  $YC_4$ . Values in parentheses correspond to the quartet electronic state, otherwise doublet electronic states. Distances are in angstroms and energies in hartrees.

= 2, 6) and dissociation energies for  $YC_2$  and  $YC_4$  were computed for the equilibrium geometries. Our computations shed light on the nature of the transition metal-carbon bonding in the yttrium carbides.

The calculations of the Gibbs free energy functions and heat content functions from statistical thermodynamics using theoretically determined molecular properties provide improved estimates of the experimentally measured enthalpies.

### Theoretical Methods and Computational Details

The calculations presented here were performed using extensive ab-initio approaches, namely, the self-consistent field (SCF), Møller-Plesset second-order perturbation (MP2),<sup>17</sup> and the density functional theory (DFT)<sup>18</sup> methods. The DFT approach has utilized the Becke<sup>19</sup> (exchange) and the Lee-Yang-Parr<sup>20</sup> (correlation) functionals. The geometry searches were made at the SCF, DFT, and MP2 levels of theory by quasi-Newton-Raphson procedure.<sup>21,22</sup>

All the calculations described here were made using the relativistic effective core potentials (RECP's) that treated all but the  $4s^2 4p^6 4d^1 5s^2$  shells in the core for yttrium<sup>23</sup> and all but the  $2s^2 2p^2$  shells in the core for the carbon atoms.<sup>24</sup> The most diffuse exponents in the original basis sets have been left uncontracted leading to the (5s4p3d) and (3p3s) valence basis sets for Y and C, respectively. The carbon basis set was supplemented with a set of six-component 3d Gaussian functions adopted from Dunning and Hay.<sup>25</sup> The above choice of the atomic basis set is based on previous experience on  $Y_n$ <sup>26</sup> and Pt-CO systems.<sup>27</sup> The MP3 optimized chemical bond in  $Y_2$

was calculated as 2.70 Å ( $^1\Sigma_g^+$  state), in close agreement with the CASSCF/MRSDCI calculations of Dai and Balasubramanian.<sup>26</sup> The MP2 calculations were performed using the spin-unrestricted Hartree-Fock method.<sup>28</sup> The projected values (free from contamination from other states) from the MP2 calculations are reported. The  $4s^2 4p^6 4d^1 5s^2$  shells of Y and the  $2s^2 2p^2$  shells of the carbon atoms were correlated in the MP2 method.

Structures obtained using the MP2 and DFT levels of theories were tested against complete active space self-consistent-field (CASSCF) and multireference configuration interaction (MRS-DCI) computations on one of the smaller clusters, namely,  $YC_2$ . The CASSCF optimization of  $YC_2$  resulted in a bent  $C_{2v}$  structure with Y-C and C-C bond distances of 2.233 and 1.277 Å, compared to the MP2 values of 2.219 and 1.282 Å, respectively. The CYC bond angles come out to be 33.2° and 33.5° at the CASSCF and MP2 levels, indicating a good agreement. The DFT results were also found to be in close agreement with the MP2 and CASSCF results. The enthalpies of formation computed using the MP2 and MRSDCI techniques are also quite close to each other. Further details can be found in ref 16.

All structures presented in this study for all  $YC_n$  clusters are minima in the potential energy surfaces. This was ensured by the computations of the second derivatives of energies.

The calculations of the thermodynamic functions have been performed at the SCF and MP2 levels of theory by applying ideal gas, rigid rotor, and harmonic oscillator approximations.<sup>29</sup> The computations were made using the Gaussian 94<sup>30</sup> codes.

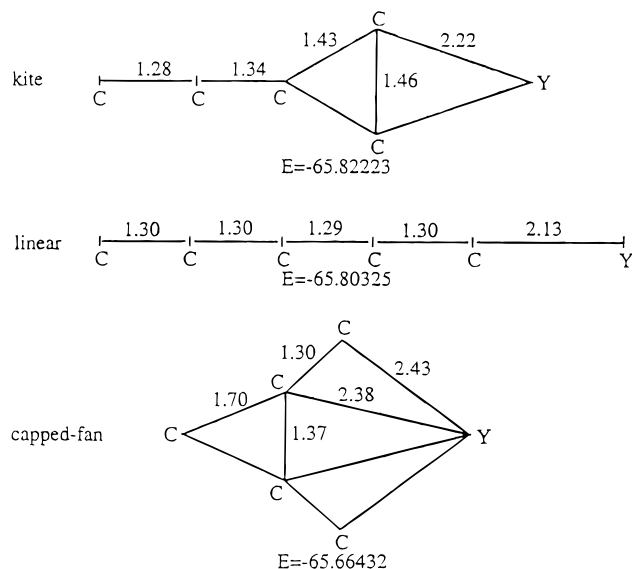
### Molecular Structures of Yttrium Carbides

The ground states of the yttrium carbides are formed from the  $Y(^2D)$  electronic state and one of the low-lying singlet or triplet states of the  $C_n$  cluster.<sup>31</sup> We considered both the quartet and doublet electronic states as candidates for the ground state. Since no spectroscopic data were available for these molecules, previous estimation of the thermodynamic properties of these species assumed their structures to be linear.<sup>12</sup> The assumption of linear structures for these molecules was based on the pseudo-oxygen character of the  $C_2$  group.<sup>4</sup> This assumption, however, is not validated by our theoretical computations.

The results for the optimized geometries of  $YC_n$ ,  $n = 2-6$ , are reported in the ensuing properties. The structures of  $YC_2$ – $YC_4$  were optimized at the MP2 level, while  $YC_5$  and  $YC_6$  were optimized within the SCF approach. The geometries which exhibited the lowest in energies for a given species were optimized further at the DFT level.

**$YC_2$ .** A detailed study of  $YC_2$  has been presented elsewhere by the authors.<sup>16</sup>  $YC_2$  has a  $C_{2v}$  equilibrium structure in a  $^2A_1$  electronic ground state. The MP2, DFT, and SCF methods gave  $R(C-Y) = 2.233, 2.233,$  and  $2.237$  Å and a C-Y-C bond angle of 33.2°, 33.2°, and 32.4°, respectively.

**$YC_3$ .** The optimized structures are presented in Figure 1. As indicated before, all structures shown in figures are local minima in the potential energy surfaces. The molecule in the doublet ground electronic state ( $^2A_1$ ) possesses a planar geometry such that the carbons form an equilateral triangle and the Y atom bonds to two of the carbon atoms, resulting in a structure which we call the "kite" structure. The second energetically lowest geometry, which we call the "fan" structure, is also planar and results from the binding of Y to all three carbon atoms. This structure is, however, 79.5 kJ/mol higher than the kite ground state for  $YC_3$ . The  $C_{3v}$  "pyramidal" structure is unstable in that if it is allowed to relax, it results in the planar kite structure of the ground state, due to the Jahn-Teller effect. The corresponding quartet state with a  $C_{3v}$



**Figure 3.** DFT optimized structures and corresponding MP2 energies ( $E$ ) for the  $YC_5$  molecule. Distances are in angstroms and energies in hartrees.

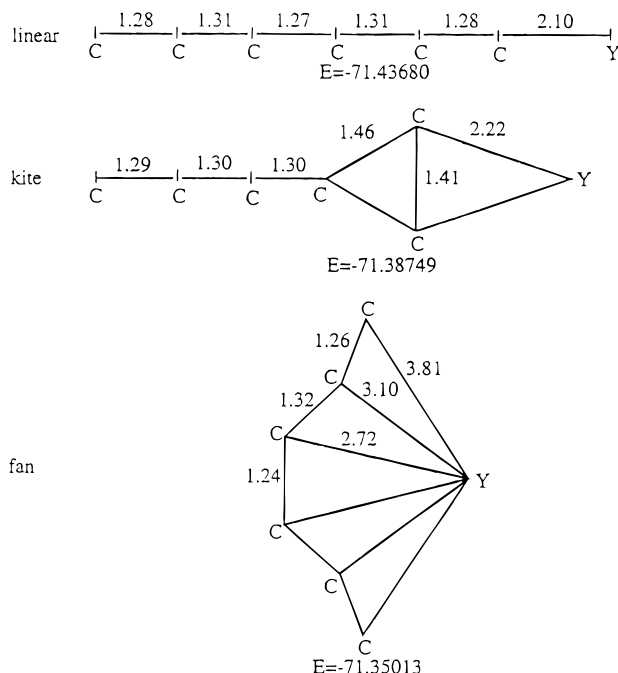
geometry is higher in energy but is stable, since the symmetry is not broken here. The "bent" structure considered in the experimental work<sup>12</sup> leads to the formation of a new C—C bond (Figure 1), and when the constraint linearity of the Y—C—C fragment is removed, the optimization leads to the planar ground state. The linear structure is 159.0 kJ/mol above the computed global minimum. All the quartet electronic states studied here are significantly higher in energy compared to the corresponding doublet states.

**$YC_4$ .** The ground state for the  $YC_4$  cluster is a  $^2A_1$  electronic state of  $C_{2v}$  symmetry with a fan structure shown in Figure 2. Based on our experience with the smaller carbides and on the fact that the linear  $YC_4$  doublet state is significantly lower than the corresponding quartet state, only doublet electronic states were studied for the other geometries. The ground state of  $YC_4$  with the fan structure is lower than the linear geometry by 158.1 kJ/mol and is significantly lower than the "kite" structure (433.2 kJ/mol). The  $C_{4v}$  "top" structure transforms into a planar "fan" structure when the  $C_{4v}$  symmetry constraint is removed. Also, the "bent" structure is high in energy, and after removing the linearity constraint of the Y—C—C branches, the optimization results in a planar fan ground state.

**$YC_5$ .** Three stable structures which are local potential minima are found for the  $YC_5$  cluster (Figure 3), among which a kite structure exhibiting a  $^2A_1$  electronic state was computed as the lowest at the MP2 level. A second stable linear structure was found to be only 49.9 kJ/mol higher than the ground state. The DFT method finds the linear structure as the lowest one. The capped-fan structure is significantly higher in energy. The MP2 level of theory does not yield a definitive ground state for  $YC_5$ , since the kite and linear structures are close in energy at this level of theory.

**$YC_6$ .** The ground state geometry of the  $YC_6$  molecule was computed to be linear ( $^2\Sigma^+$ ). Two other stable structures shown in Figure 4, namely, the kite and fan structures, are above the ground state by 129.5 and 227.6 kJ/mol, respectively.

Experimental data indicate that for the pure elemental carbon clusters  $C_n$  with  $2 \leq n \leq 9$ , the linear chains are the most stable.<sup>32</sup> The attachment of the Y atom perturbs carbon chains containing up to four carbon atoms which are involved in direct binding. The formation of a linear chain (tail) from the atoms that are not directly involved in binding with Y seems to be a



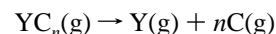
**Figure 4.** DFT optimized structures and corresponding MP2 energies ( $E$ ) for the  $YC_6$  complex. Distances are in angstroms and energies in hartrees.

preferable pathway for the bonding of  $YC_n$  clusters for larger values of  $n$ , in analogy with the pure carbon clusters.

Three general features are noted for the  $YC_n$  clusters on the basis of the Y—C bond lengths as  $n$  increases. The linear structure for a given cluster has the shortest Y—C bond. The Y—C bonds in the kite structure are approximately 0.2 Å longer than the corresponding bond lengths in the linear structures for a given  $YC_n$ . The Y—C bonds are again longer by roughly 0.1 Å in the fan structures compared to the linear structures, the only exception being the fan structure of  $YC_3$ . However, in the smaller  $YC_3$  cluster, multiple Y—C bonds exist as a result of one fewer carbon atom. Although the growth of the structures is systematic within a given pattern, the ground states belong to different patterns for different  $n$ , for smaller values of  $n$ . In larger species such as  $YC_5$  and  $YC_6$ , the carbons not bonded to Y prefer to form linear chains. In the case of  $YC_6$ , a linear structure is favored, while in the  $YC_5$  cluster, the linear and kite structures are nearly degenerate. Consequently, in smaller structures, bonding of the Y atom with multiple carbon atoms seems to be a predominant factor for the determination of the lowest energy structure, while for the larger structures the carbon—carbon chain stabilization energy through extension of conjugation is the predominant factor for the structure determination. The smaller stabilization of even carbon clusters compared to the odd ones<sup>33</sup> may be a contributing factor for the preferential formation of the fan structure for the  $YC_4$  cluster. All of the optimal structures are planar, indicating the possibility of  $\pi$  bonds in these structures.

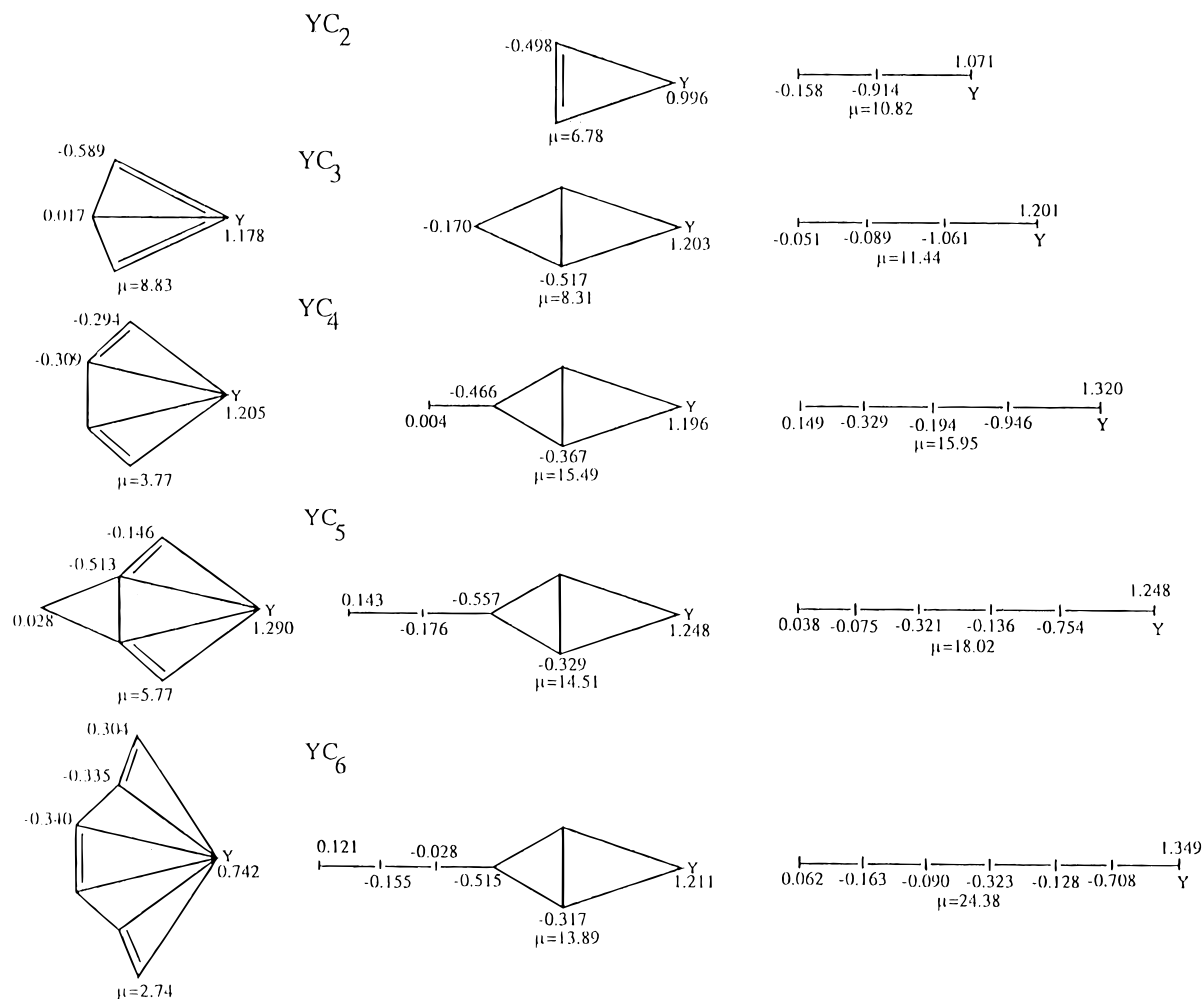
### Computation of Thermodynamic Properties and Comparison with Experiment

The theoretical atomization energies were calculated for the determined ground states of  $YC_n$  for the following process:



The enthalpy of the reaction

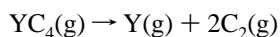
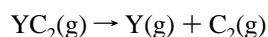




**Figure 5.** Atomic charges and dipole moments (in debye) for fan, kite, and linear patterns of YC<sub>n</sub> (*n* = 2–6).

was subsequently calculated by applying the sublimation energy of graphite. The calculated and experimental atomization enthalpies are presented in Table 1. As seen from Table 1, the agreement is very good when the MP2 energies obtained from the MP2 optimized structures are applied for the enthalpy calculations of YC<sub>2</sub> to YC<sub>4</sub>. The use of the MP2 energies calculated at the DFT and SCF optimized geometries underestimates the atomization energies, although the DFT geometries are close to the MP2 geometries. The results obtained by using the SCF geometries, as expected, are much lower but are in accord with the anticipated trends. The inclusion of correlation energy is essential for the proper computation of the atomization energies. The zero-point vibrational energy correction lowers the calculated atomization enthalpies (28.1 kJ/mol for YC<sub>2</sub> to 75.5 kJ/mol for YC<sub>6</sub>). The computed enthalpies for the formation of YC<sub>n</sub>(g) from Y(g) and *n*C(graphite) using the sublimation energy of graphite are in good agreement with the experimental data (see Table 1).

The dissociation energies of YC<sub>2</sub> and YC<sub>4</sub> for the following processes:



are computed at the MP2 level of theory as 622.2 and 267.9 kJ/mol for YC<sub>2</sub> and YC<sub>4</sub>, respectively. These values are within the experimental error bars for the measured values.<sup>9,12</sup>

### Nature of the Chemical Bond and Its Influence of the Molecular Topology

The Y–C bonds have considerable ionic character arising from the transfer of an electron from the yttrium atom to the carbon chain. The stabilization of the Y center depends on the ability of the carbon fragment to accept the electronic density. The immediate neighbors of Y are the most affected by the Y + C<sub>n</sub> reaction, although the charge distribution of the carbon chain is complicated, and even the carbon atoms not directly involved in bonding are influenced by the operation of resonance (Figure 5). The transferred electronic density from the yttrium atom is roughly equally distributed between the nearest neighbors, and this distribution, in turn, leads to considerable stabilization of nonlinear structures. However, this mechanism competes with the stabilization mechanism of the carbon chain not directly bonded to the Y center through resonance. As the chain becomes longer, a linear structure prevails over other structures such as the kite and fan structures. For smaller number of carbon atoms the extension of conjugation is not sufficient enough to stabilize the linear structure compared to multicenter bonded structures such as the fan and kite structures. In the case of YC<sub>6</sub>, the linear structure becomes the preferred one.

The  $\pi$  orbitals of Y play an important role as electron acceptors, and the bonding can be described within the  $\sigma$  donation– $\pi$  back-donation model with “back-donation” as large as 0.4 electron in the YC<sub>2</sub> case. As an example, the difference density maps are presented for the YC<sub>3</sub> molecule (Figure 6).

**TABLE 1: Atomization Enthalpies  $\Delta H_{a,0}^\circ$  and Reaction Enthalpies  $\Delta H_0^\circ$  for the Reaction  $Y(g) + nC(\text{graphite}) = YC_n(g)$  (Energies in kJ/mol)**

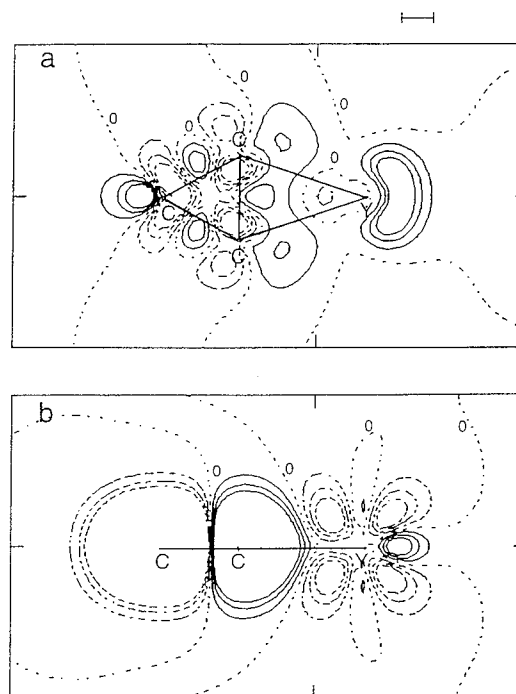
species	method	$\Delta H_{a,0}^\circ$		$\Delta H_0^\circ$	
		theoret	exper <sup>a</sup>	theoret <sup>b</sup>	exper
YC <sub>2</sub>	MP2	1216.7	1225 ± 8	205.7	197 ± 5
	MP2(DFT) <sup>c</sup>	1215.7			
	MP2(SCF) <sup>d</sup>	1212.0			
	DFT	1167.1			
	SCF	791.5			
YC <sub>3</sub>	MP2	1712.5	1757 ± 12	421.1	377 ± 10
	MP2(DFT)	1712.2			
	MP2(SCF)	1558.7			
	DFT	1642.8			
	SCF	1017.3			
YC <sub>4</sub>	MP2	2491.4	2484 ± 10	360.8	361 ± 8
	MP2(DFT)	2489.8			
	MP2(SCF)	2396.4			
	DFT	2379.3			
	SCF	1678.9			
YC <sub>5</sub>	MP2(DFT)	2875.4	3057 ± 15	680.6	499 ± 10
	MP2(SCF)	2866.6			
	DFT	2798.8			
	SCF	1900.8			
	MP2(DFT)	3537.4	3731 ± 20	729.8	536 ± 15
YC <sub>6</sub>	MP2(SCF)	3533.5			
	DFT	3473.1			
	SCF	2362.8			

<sup>a</sup> From ref 12. <sup>b</sup> Using  $\Delta H_{f,0}(\text{graphite}) = 711.2 \text{ kJ mol}^{-1}$ , ref 34.<sup>c</sup> MP2 calculations using DFT optimized geometry. <sup>d</sup> MP2 calculations using SCF optimized geometry.

The gain of electronic density outside  $\sigma$  bonds is quite visible. The  $\pi$  bonds in the carbon ring stabilize the planar structures.

### Thermodynamic Functions

The theoretically determined enthalpies depend mainly on the quality of the electronic energy calculations since the

**Figure 6.** Electron density difference maps between YC<sub>3</sub> and its subunits (Y + 3C) in the molecular plane (a) and the perpendicular  $\sigma_v$  plane (b). The spacing between the contours is 0.01 electron/bohr.<sup>3</sup> The contours are labeled with zeros, while solid lines indicate enhancement of electronic density.

techniques do not include electron correlation effects to the same extent. Experimental results, too, may depend on the molecular structures, which are needed for the estimation of the Gibbs free energy and heat content functions. Thermodynamic properties may be calculated from the spectroscopic data, but in the absence of such data, these properties are estimated from

**TABLE 2: Gibbs Energy Functions,  $GEF = (G^\circ_T - H^\circ_0)/T$ , and Heat Content Functions,  $\Delta H = H^\circ_T - H^\circ_0$ , Calculated for  $n = 2-6$  of YC<sub>n</sub> (GEF in J/mol,  $\Delta H$  in kJ/mol)**

species	method		temp, K						
			298	2000	2200	2400	2600	2800	3000
YC <sub>2</sub>	SCF	GEF	-226.1	-317.5	-322.4	-326.9	-331.1	-335.0	-338.7
		$\Delta H$	13.26	102.2	113.6	125.0	136.4	147.9	159.4
		$\Delta H$	12.01	103.4	114.9	126.3	137.8	149.3	160.8
	MP2	GEF	-230.7	-304.8	-310.4	-322.4	-326.6	-330.5	-334.2
		$\Delta H$	10.6	101.8	113.4	124.9	136.4	147.9	159.4
	EST <sup>b</sup>	GEF	-221.8	-311.1	-316.1	-321.3	-325.9	-330.2	-334.2
		$\Delta H$	10.6	111.6	124.0	136.5	149.0	161.5	174.0
		$\Delta H$	12.7	140.5	156.8	173.2	189.6	206.0	222.4
	SCF <sup>a</sup>	GEF	-249.5	-360.3	-367.2	-373.5	-379.4	-384.9	-390.1
		$\Delta H$	13.1	142.9	159.3	175.7	192.1	208.6	225.1
YC <sub>3</sub>	SCF	GEF	-248.3	-356.1	-362.8	-369.0	-374.8	-380.3	-385.4
		$\Delta H$	12.7	140.5	156.8	173.2	189.6	206.0	222.4
		$\Delta H$	12.7	141.5	157.8	174.2	190.6	207.1	223.5
	MP2	GEF	-248.7	-357.3	-364.1	-370.4	-376.2	-381.7	-386.8
		$\Delta H$	12.7	141.5	157.8	174.2	190.6	207.1	223.5
	EST <sup>b</sup>	GEF	-234.1	-346.5	-353.6	-360.2	-366.4	-372.1	-377.5
		$\Delta H$	12.3	148.6	165.8	183.0	200.3	217.7	235.1
		$\Delta H$	12.3	148.6	165.8	183.0	200.3	217.7	235.1
	SCF <sup>a</sup>	GEF	-254.6	-386.7	-395.2	-403.1	-410.4	-417.3	-423.8
		$\Delta H$	14.7	176.6	197.5	218.6	239.7	260.9	282.1
YC <sub>4</sub>	EST <sup>b</sup>	GEF	-246.1	-382.0	-391.0	-399.2	-406.9	-414.2	-420.9
		$\Delta H$	14.2	185.7	207.7	229.8	252.0	274.2	296.5
		$\Delta H$	14.2	185.7	207.7	229.8	252.0	274.2	296.5
	SCF	GEF	-270.2	-429.4	-439.8	-449.4	-458.4	-466.8	-474.8
		$\Delta H$	17.5	216.2	242.0	268.0	294.0	320.1	346.3
		$\Delta H$	17.5	216.2	242.0	268.0	294.0	320.1	346.3
YC <sub>5</sub>	EST <sup>b</sup>	GEF	-257.9	-417.5	-428.2	-438.2	-447.5	-456.2	-464.4
		$\Delta H$	16.1	222.9	249.7	276.6	303.6	330.7	357.9
		$\Delta H$	16.1	222.9	249.7	276.6	303.6	330.7	357.9
	SCF	GEF	-289.3	-484.8	-497.4	-509.1	-520.0	-530.2	-539.8
		$\Delta H$	21.8	262.2	293.5	324.9	356.5	388.2	420.0
		$\Delta H$	21.8	262.2	293.5	324.9	356.5	388.2	420.0
YC <sub>6</sub>	EST <sup>b</sup>	GEF	-269.7	-453.0	-465.5	-477.1	-488.0	-498.2	-507.8
		$\Delta H$	18.1	260.1	291.7	323.4	355.3	387.3	419.3
		$\Delta H$	18.1	260.1	291.7	323.4	355.3	387.3	419.3
	SCF	GEF	-289.3	-484.8	-497.4	-509.1	-520.0	-530.2	-539.8
		$\Delta H$	21.8	262.2	293.5	324.9	356.5	388.2	420.0
		$\Delta H$	21.8	262.2	293.5	324.9	356.5	388.2	420.0

<sup>a</sup> Frequencies scaled by 0.89. <sup>b</sup> From ref 9.

the assumed molecular parameters. The values of thermodynamic functions are less sensitive to the assumed structures than the electronic energies. Table 2 presents the Gibbs free energy and heat content functions calculated for the located ground state and estimated results for the experimental enthalpies.<sup>12</sup> These functions can be used for the calculation of the enthalpy of the  $Y(g) + nC(\text{graphite}) = YC_n(g)$  reactions within the second and third laws. Despite the difference between the structures assumed at the experimental level and the theoretical ground states, the agreement between the two sets of thermodynamic functions is reasonable.

The experimentally estimated thermodynamic functions can be corrected for the assumed erroneous molecular structures as

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

which gives the correction to the atomization energies calculated via the third law method. The largest corrections, with the Gibbs free energy functions from Table 2 applied, are 12.6 kJ/mol for  $YC_2$ , 31.2 kJ/mol for  $YC_5$ , and 96.0 kJ/mol for  $YC_6$ .

## Conclusions

Although there are several experimental studies on the transition-metal carbides, little theoretical work has been done on such molecules. The present theoretical study shed light on the equilibrium geometries, energies, and the nature of bonding of  $YC_n$ . Three different types of stable molecular structures were optimized for these species. Our computations showed that for smaller yttrium carbide clusters bonding between the yttrium atom and several carbon atoms is favored, while for the larger clusters the extension of conjugation of the carbon chains becomes the predominant factor. Consequently, smaller  $YC_n$  clusters form structures in which the Y atom is multiply bound to several carbons simultaneously such as the fan and kite structures while larger clusters such as  $YC_6$  favor a linear ground state structure.

The theoretically computed thermodynamic atomization, dissociation energies, and enthalpies of the ground state structures are found to be in excellent agreement with the experimental  $Y(g) + nC(\text{graphite}) = YC_n(g)$  reaction enthalpies, atomization energies of  $YC_n$ , and available dissociation energies. The calculated enthalpies are sensitive to the inclusion of the electron correlation energy, and at the very least DFT or MP2 levels of theory have to be applied to ensure qualitative agreement with experiment.

The choice of molecular structure does not significantly influence the experimental enthalpies because the thermodynamic functions are similar for different geometries. Theoretically calculated thermodynamic functions (quantum-chemical approach combined with statistical thermodynamics) agree reasonably well with the estimated values, which were applied for the experimental evaluation of thermodynamic data. Since different structures of  $YC_n$  have been considered in both experimental and theoretical studies, the experimental results are found to change slightly when the correct structures of the clusters were used.

The Y–C bonds were found to be strongly ionic, and the main difference between the various structures comes from the delocalization of the transferred electronic charge from Y to C over the carbon chain. The binding per Y–C bond is the

strongest in the linear case, but because the number of bonds is larger in the kite and fan structures, the Y bonding with multiple carbons favors the fan and kite structures for the smaller clusters.

**Acknowledgment.** This research was supported in part by the U.S. Department of Energy under Grant DEFG0286ER13358. We thank the San Diego Supercomputer Center for providing computer time on a Cray C90 system. S.R. thanks the Department of Chemistry, Technical University of Wroclaw, for a leave of absence which made this cooperation possible.

## References and Notes

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