The Nature of Bonding in WC and WN

Xue Mei GAO[1]*, Shi Xi LIU[2], Xiao Guang XIE[1], Huai CAO[2], Shu Shan DAI[1]

[1]Department of Chemistry, Yunnan University Kunming 650091
[2]Modern Biological Center, Yunnan University Kunming 650091

Abstract: The nature of bonding in the title compounds has been studied by using CASSCF and FOCI techniques. The ground states of WC and WN are found to be $^3\Delta$ and $^4\Sigma^-$ state arising primarily from:$\ldots1\sigma^2 2\sigma^2 1\pi^4 1\delta^1 3\sigma^1$ and $\ldots1\sigma^2 2\sigma^2 1\pi^4 1\delta^2 3\sigma^1$ configuration respectively. WC shows a strong character of covalent bond while WN have obvious character of ionic bond and the dissociation energy of WN is larger than that of WC (6.15 and 5.41 eV respective).

Keywords: WC and WN, nature of bonding, molecular constants, CASSCF, FOCI

The theoretical study of small molecules containing transition metal atoms is one of the most active areas in quantum chemistry[1]. Very extensive studies have been done on first and second row transition metal hydrides[2,3], oxides[4-6] and the transition metal dimers[7-9]. But theoretical studies on the third row transition metal compounds are comparatively scarce.

Tungsten is an important element for catalytic reactions, and the knowledge of the interaction between W and C/N atom has basis importance for the understanding of such catalytic aspects. The spectroscopic investigation of WN has been reported[10]. But there is no *ab initio* predictions reported for properties of WC and WN. In the present work we describe the nature of the bonding in WC and WN through *ab initio* calculations by using CASSCF and FOCI techniques and calculate their molecular constants.

Methods

The calculations were firstly carried out for the optimizations of the different multiplicity states of WC and WN by using HF method, followed by the CASSCF optimization calculations. Then, the first order CI (FOCI) calculations were done to include the higher-order electronic correlation effects. The relativistic compact effective potential (RCEP) and its matching basis set[11] was used for W atom and for C and N atoms, 6-31G(d) basis set was used. The CASSCF active space consists of 10/11 electrons and 10 orbitals for WC/WN resulting in thousands of spin configuration functions. The FOCI method included all configurations in the CASSCF plus configurations obtained by distribution of 9/10 electrons (for WC/WN) in the internal space and one electron in the orthogonal external space in all possible ways including up to three-to-five hundred

thousands spin configuration functions.   The calculations of at least six single points lying near equilibrium geometry within 0.005Å were performed to determine the molecular constants based on Morse's potential energy function.   All calculations were performed with PC GAMESS 5.0[12] running on PII PC computer.

Results and Discussion

It is found from the calculations that the ground states of WC and WN are $^3\Delta$ and $^4\Sigma^-$ state arising primarily from: $\ldots1\sigma^22\sigma^21\pi^41\delta^13\sigma^1$ and $\ldots1\sigma^22\sigma^21\pi^41\delta^23\sigma^1$ configuration respectively which agree with the optical spectra of WN[10].   The low-lying $^1\Sigma^+$ and $^2\Delta$ states of WC and WN have the dominant configuration $\ldots1\sigma^22\sigma^21\pi^43\sigma^2$, and $\ldots1\sigma^22\sigma^21\pi^41\delta^13\sigma^2$.   They lie higher than their corresponding ground state only by 0.48 and 0.67eV respectively and their dominant configurations come from the transition of one electron from 1δ to 3σ orbital of their corresponding ground state resulting in the pair of electrons in 3σ orbital.   This indicates that the 3σ orbital is something like an anti-bonding orbital.   But the ground states of WC and WN having the configuration of $1\delta^13\sigma^1$ and $1\delta^23\sigma^1$ rather than that of $1\delta^2$ and $1\delta^3$ implies the near degeneracy of the 1δ and 3σ orbital.   The calculated molecular constants are listed in **Table 1**.

Table 1   The calculated molecular constants of WC and WN and their experimental values[10]

			Re(Å)	De(eV)	Te(eV)	We(cm^{-1})	XeWe(cm^{-1})	B0(cm^{-1})
WC	X$^3\Delta$	CASSCF	1.744	3.71	0.0	968.5	7.8	0.4915
		FOCI	1.747	5.43	0.0	937.0	5.0	0.4897
		Expt.						
	$^1\Sigma^+$	CASSCF	1.767	3.06	0.65	970.0	9.5	0.4789
		FOCI	1.766	4.93	0.48	971.2	5.9	0.7970
		Expt.						
WN	X$^4\Sigma^-$	CASSCF	1.696	4.38	0.0	1026.1	7.5	0.4504
		FOCI	1.700	6.15	0.0	1022.2	5.3	0.4479
		Expt.	1.678	5.86				0.4664
	$^2\Delta$	CASSCF	1.847	3.58	0.80	1069.6	9.9	0.4549
		FOCI	1.812	5.48	0.67	1060.3	6.4	0.4523
		Expt.						

De is obtained from the dissociation limits for the processes: WC→W(^{5}D) + C(^{3}P); WN→W(^{5}D) + N(^{4}S).

The calculated molecular constants by the CASSCF method are in agreement with those by FOCI method except for the dissociation energy, which is significantly improved by the later method including higher-order electronic correlation effects and comparable with the experimental value.   It is well known that the valence CASSCF procedure overestimates the effect of configurations with anti-bonding orbitals occupied, yielding, therefore, a too long distance and too small bond energy.   Therefore the higher-order electron correlation effects must be included.   But for the transition energy (Te), the calculated values at both of these levels are very close.   This implies that the CASSCF method is a valuable tool to qualitatively describe the electronic states of the transition-metal-contained compounds.   The same conclusion has been made by our another paper[13].   The low-lying $^1\Sigma^+$ and $^2\Delta$ states of WC and WN lie higher than their

corresponding ground state only by 0.48 and 0.67eV respectively at the FOCI level and this indicates a high density of low-lying molecular electronic states for WC and WN. This is reasonable because the energy separation between W atomic states arising from the $5d^5 6s^1$ and $5d^4 6s^2$ configurations is small and W atomic spin-orbit interaction is large. Although the relativistic effect correction of the inner shell electrons is include in the relativistic effective potentials, the spin-orbit interaction of the valence electrons must be considered for the accurate theoretical calculations of the transition-metal-contained compounds, especially for the 5d-transition metals. This is the defect of this work.

Table 2 The population analysis and orbital analysis of the valence orbitals of the ground state ($^3\Delta$) of WC from the nature molecular orbital (at FOCI level)

Orbital	Atomic population		Overlap population	Orbital analysis %					Occupation
				W			C		
	W	C	WC	s	p	d	s	p	number
1σ	0.36	1.49	0.12	25	10	25	35	5	1.97
2σ	0.81	0.85	0.23	7	9	47	15	22	1.89
3σ	0.98	0.03	0.68	43	11	37	5	4	1.00
1π	1.95	1.16	-0.01		11	51		38	3.79
1δ	1.00	0.00	0.0			99			1.00
Others	0.12	0.23							0.35
Total	5.22	3.76	1.02						10.0

Table 3 The population analysis and orbital analysis of the valence orbitals of the ground state ($^4\Sigma^-$) of WN from the nature molecular orbitals (at FOCI level)

Orbital	Atomic population		Overlap population	Orbital analysis %					Occupation
				W			N		
	W	N	WN	s	p	d	s	p	Number
1σ	0.20	1.72	0.06	15	19	16	48	2	1.98
2σ	0.66	1.12	0.14	17	8	39	8	28	1.92
3σ	1.00	0.0	-0.01	48	7	41	4		1.00
1π	1.34	2.03	0.42		12	39		49	3.79
1δ	2.00	0.0	0.0			99			2.00
Others	0.11	0.20							0.31
Total	5.22	5.17	0.61						11.00

The population analysis and orbital analysis of the valence orbitals of WC and WN for the ground states from the nature molecular orbitals (at FOCI level) is presented in **Table 2** and **Table 3**. The 1σ orbital of the ground state of WC and WN is mainly composed of C (2s) and W (5d & 6s). But the orbital occupation mainly comes from electrons of 2s orbital of C and N atom and the overlap population analysis shows this 1σ orbital making small contributions to the bond formed between W and C/N atom. The 2σ orbital is composed of W (6s & $5d\sigma$) and C ($2p\sigma$)/N ($2p\sigma$). From the orbital analysis, it is expected that the hybridization of W (6s) and W (5d) occurs. The σ (sd+) hybrid orbital is polarized towards C or N atom and forms a strong bond. The 1π orbital is composed of W ($5d\pi$) and C ($p\pi$)/N ($p\pi$). The composition of this orbital and population analysis is evidently suggestive of a strong π-bond formed between W and C/N. The 3σ orbital is predominantly composed of W σ (sd-) and the orbital occupation mainly coming from the electrons of W atom and the overlap population

being negative indicates the 3σ orbital is something like an anti-bonding orbital. Compared with that of WN, the overlap populations of 2σ and 1π orbitals of WC are larger and it strongly demonstrates that the bonds formed between W and C is stronger than that of WN.   But the calculated dissociation energies of them show the reverse results.   This can be explained from the atomic orbital population analysis which shows that WN has the obvious character of ionic bond and it is this feature of ionic bond makes the dissociation energy of WN larger than that of WC.

The atomic orbital populations of the ground states of WC and WN (at FOCI level) are (W: $5d^{4.49}6s^{0.87}6p^{0.37}$;   C: $2s^{1.78}2p^{2.49}$) and (W: $5d^{4.62}6s^{0.74}6p^{0.17}$;   N: $2s^{2.01}2p^{3.47}$) respectively.   The total gross populations indicate the transfer of electronic charge from W to C and N (0.27 and 0.48 electrons for WC and WN respectively).   This demonstrates that WN has obvious character of ionic bond.   The W (6s) populations in WC and WN are smaller than 1.0 and W (5d) populations are larger than 4.0, implying that the promotion of electrons from 6s to 5d orbitals occurs when the bond formed between W and C or N.

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