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Structure and thermodynamic stability of the OsC and OsC_2 molecules by theoretical calculations and by Knudsen cell mass spectrometry

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Knudsen cell mass spectrometric equilibrium measurements together with theoretical computations have been employed to gain structural and thermodynamic information of the OsC and OsC_2 molecules. Several levels of theory have been applied to determine the structures, molecular parameters, and physico-chemical properties of OsC(g) and $OsC_2(g)$, and their singly charged ions. Complete active space self-consistent field (CASSCF) calculations were performed on the apparent $^3\Sigma^-$ ground state and first $^3\Delta$ excited state of OsC. From the analyzed gaseous equilibria and the thermal functions calculated from the computed molecular parameters, the following atomization enthalpies, $\Delta_a H_0^o(\mathrm{OsC},g)$ and $\Delta_a H_0^o(\mathrm{OsC}_2,g)$, and enthalpies of formation, $\Delta_f H_{298.15}^o(\mathrm{OsC},g)$ and $\Delta_f H_{298.15}^o(\mathrm{OsC}_2,g)$, in kJ mol^{-1}, have been obtained: OsC, 605.6±14.0 and 895.4±14.0; OsC_2, 1154.6±18.0 and 1059.5±18.0. The results have been compared with those for the other platinum metal carbides and oxides. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1390504]

I. INTRODUCTION

Platinum metals and their alloys are important components of heterogeneous catalysts used in petrol reforming, in catalytic converters in cars, and in coal gasification and liquefaction.[1] Therefore the knowledge of the interaction between platinum-metal atoms and carbon atoms is of considerable fundamental importance towards the understanding of such catalysis.

The platinum-metal monocarbides RuC, RhC, IrC, and PtC were first investigated by optical spectroscopy by Scullman and co-workers[2–5] and by Knudsen effusion mass spectrometry by Drowart and associates.[6,7] The first dicarbides of these molecules have been observed under equilibrium conditions by Gingerich and co-workers[8,9] in concentrations between 10^{-2} and 10^{-3} of that of the corresponding monocarbide. Further high-temperature mass spectrometric measurements followed: RuC,[10] OsC and OsC_2,[11] $PtC_n(n=1-5)$ and $IrC_n(n=1-4)$,[12] RhC,[13] and RuC.[14]

A steady stream of *ab initio* calculations has been performed on platinum-metal monocarbides since 1982 to elucidate the electronic structure, nature of bonding, and molecular parameters of their ground state and low-lying excited electronic states: PdC,[15–21] RuC,[14,17,18,22] RhC,[13,17,18,23] IrC,[24] and PtC.[25] In recent years there has been renewed interest in optical spectroscopic studies of platinum-metal monocarbides: RuC,[26,27] RhC,[28,29] PdC,[30] IrC,[31] and PtC.[32,33]

In the present investigation we report our results for OsC and OsC_2 from density functional and *ab initio* calculations and from high-temperature mass spectrometric measurements. Preliminary values of the atomization energies have previously been published.[11]

II. THEORETICAL INVESTIGATIONS

No previous theoretical investigations have been carried out on the OsC and OsC_2 molecules. In this study, *ab initio* and density functional theory calculations have been performed on OsC(g), $OsC^+(g)$, $OsC^-(g)$, $OsC_2(g)$, $OsC_2^+(g)$, and $OsC_2^-(g)$ to investigate their structures, molecular parameters, physico-chemical properties, and nature of bonding. The results from the calculations have been used to calculate the thermal functions needed to evaluate the mass spectrometric equilibrium data and thermodynamic properties of OsC and OsC_2.

All calculations were performed using the GAUSSIAN 98 suite of programs[34] with the correlation consistent polarized valence double-ζ basis set (cc-pVDZ) on carbon, and the Stuttgart triple-ζ basis set with a small core ($1s2s2p3s3p3d4s4p4d$) relativistic effective core potential (ECP) on osmium.[35] Five levels of theory were used in this investigation: (1) Hartree–Fock (HF) theory, (2) density functional theory using the Becke three-parameter exchange functional and the Lee–Yang–Parr correlation functional (B3LYP), (3) Møller–Plesset second-order perturbation theory (MP2), (4) coupled cluster singles and double excitations (CCSD), and (5) coupled cluster singles and double excitations with the inclusion of perturbative triples [CCSD(T)]. Full geometry optimizations were performed at all five levels of theory for the neutral species. Full geometry optimizations were performed at the CCSD(T) level of theory for the ion species. All calculations with the multiplicity higher than 1 were optimized with unrestricted (U) spin; the α molecular orbitals containing the spin up electrons are optimized independently from the β molecular orbitals containing the spin down electrons. Lastly, complete active space self-consistent field (CASSCF)[36] calculations

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TABLE I. The optimized molecular parameters for the OsC molecule: energy (in hartree), bond distance (in Å), and vibrational frequency (in cm^{-1}) at the CCSD(T) level of theory.

Method	State	E	ΔE[a]	$r_{\text{Os-C}}$	ν
CCSD(T)	$^1\Sigma^+$	−127.8834	133.4	1.70	967
	$^3\Delta$	−127.9241	26.6	1.69	1055
	$^3\Sigma^-$	−127.9342	0.0	1.71	1057
	$^5\Pi$	−127.8788	145.4	1.73	948
	$^7\Sigma^+$	−127.7963	362.1	1.84	806

[a] ΔE is in kJ mol^{-1}.

were performed for OsC with a multiplicity of 3. Details of all theoretical calculations for all species studied will be reported in a subsequent publication.

A. OsC theoretical results

Four spin states were investigated for OsC ($S=0$, 1, 2, and 3). Table I lists the optimized molecular parameters and energy obtained at the CCSD(T) level of theory for the four spins available. The ordering of the states studied changed significantly depending on the level of theory used. At the CCSD and CCSD(T) level of theory, the $^3\Sigma^-$ is the lowest energy state followed by $^3\Delta$, $^1\Sigma^+$, $^5\Pi$, and $^7\Sigma^+$ in increasing order, and is lower than the $^3\Delta$ state by 20.6, and 26.6 kJ mol^{-1}, respectively.

Due to the small energy difference between the $^3\Sigma^-$ and the $^3\Delta$ states, CASSCF calculations were performed to determine if the $^3\Sigma^-$ state is indeed lower in energy than the $^3\Delta$ state. CASSCF calculations were performed with two different active spaces: 6 e^- in six orbitals, $1\sigma 2\sigma 1\delta 3\sigma 4\sigma$ (6,6), and 10 e^- in ten orbitals, $1\pi 1\sigma 2\sigma 1\delta 3\sigma 4\sigma 2\pi$ (10,10). Table II lists the natural orbital (NO) occupations obtained at the highest level of CASSCF calculations similar to RuC.[18,22] The chemical bond in OsC is approximately a triple bond, consisting of two π and one σ bond. The $^3\Sigma^-$ state is 19.7 kJ mol^{-1} lower in energy than the $^3\Delta$ state with the (10,10) active space, and is possibly the ground state.

The atomization energy of OsC calculated at the CCSD(T) level of theory is 5.63 eV. Since Os is a third row transition metal, spin-orbit coupling becomes a significant factor and, since it was not included in these calculations, it could cause errors of around 0.5 eV in the calculation of the atomization energy. The experimentally determined $\Delta_a H_0^{\circ}(\text{OsC},g)$ is (6.28±0.15) eV, in reasonable agreement with the computations.

The cation and anion of OsC were optimized at CCSD(T) level of theory. The Os–C bond distance in OsC^+ was calculated to be 1.67 Å in the $^2\Delta$ state and 1.69 Å in the $^2\Sigma^+$ state. The $^2\Delta$ state is 24.4 kJ mol^{-1} lower in energy than the $^2\Sigma^+$ state. The ionization energy of the $^3\Sigma^-$ state of OsC to $^2\Delta$ OsC^+ at the CCSD(T) level is 8.54 eV, which is within the experimental range (8.3±0.5) eV. The Os–C bond distance in OsC^- was calculated to be 1.69 Å for the $^2\Delta$ state. The electron affinity for OsC was calculated to be 1.6 eV. Table III lists the molecular parameters calculated at the CCSD(T) level of theory for the lowest lying states of OsC, OsC^+, and OsC^-.

TABLE II. Complete active space self-consistent field (CASSCF) energies, in hartree, and natural orbital (NO)[a] occupations for (10,10) active space calculations for OsC at a bond distance of 1.7 Å.

	CASSCF(10,10)	
State	Energy	Natural orbitals
$^3\Sigma^-$	−127.7172	$1\sigma^{1.97}2\sigma^{1.92}1\pi^{3.80}1\delta^{2.00}2\pi^{0.20}3\sigma^{0.10}4\sigma^{0.07}$
$^3\Delta$	−127.7097	$1\delta^{2.99}1\sigma^{1.93}1\pi^{3.80}2\sigma^{1.00}2\pi^{0.20}3\sigma^{0.07}4\sigma^{0.01}$

[a] Molecular orbitals are numbered starting with the valence orbitals.

B. OsC_2 theoretical results

For the OsC_2 molecule eight different structures with four different spins ($S=0$, 1, 2, 3) were investigated. Figure 1 shows the eight geometries investigated at varying levels of theory and spins. At all levels of theory, except HF, the lowest minimum was calculated to be a $^1A_1$ state with the general structure labeled A in Fig. 1. The optimized molecular parameters and energy for the apparent ground state of OsC_2 at the CCSD(T) level of theory employed are the bond distances, in Å, $r_{\text{Os–C}}=1.75$, $r_{\text{C–C}}=1.79$; the angle $\angle$C–Os–C $=61.5°$; the vibrational frequencies, in cm^{-1}, 195 (bending), 913 (symmetric stretching), 1060 (antisymmetric stretching); and the energy, in hartree, is −165.8902.

The atomization energy of OsC_2 calculated at the CCSD(T) level of theory is 10.9 eV. The experimentally determined $\Delta_a H_0^{\circ}(\text{OsC}_2,g)$ value is (11.97±0.19) eV, in reasonable agreement with the computed value.

The cation and anion of OsC_2 were optimized at the CCSD(T) level of theory and they were found to be a $^2A_1$ state. The ionization energy of the $^1A_1$ OsC_2 state at the CCSD(T) level of theory is 8.49 eV, again within the error limits of the experimental value of (8.9±0.5) eV. The electron affinity of OsC_2 was calculated to be 0.7 eV. Table III lists the molecular parameters calculated at the highest level of theory for the OsC_2, OsC_2^+, and OsC_2^- apparent ground states.

III. EXPERIMENT

The measurements of the ion currents of Os^+, C^+, OsC^+, and OsC_2^+ under equilibrium conditions were performed with a Nuclide Corporation 12-90 HT single focusing magnetic deflection type mass spectrometer. Details of the instrument and experimental procedures used in this investigation have been described elsewhere.[37] The graphite Knudsen cell, inserted in a tantalum Knudsen cell, was charged with a mixture of cerium, rhodium, ruthenium, and osmium to which graphite powder in substantial excess was added to insure unit activity of carbon during the measurements. The cell was heated by radiation by a tungsten coil resistor. Temperatures were measured by sighting a calibrated optical pyrometer at a blackbody hole at the bottom of the tantalum cell. Appropriate window and prism corrections were applied. The energy of the ionizing electrons was 20 eV, the emission current was regulated at 1.0 mA, the ion-accelerating voltage was 4.5 kV, and the electron multiplier was operated at −2 kV. The identification of the ionic species as parent ions was accomplished by the measurement of

TABLE III. Molecular parameters calculated at the CCSD(T) level of theory for OsC, OsC^+, OsC^-, OsC_2, OsC_2^+, and OsC_2^- together with the ionization energy (IE), in eV, electron affinity (EA), in eV, zero-point energy (ZPE), in kJ mol^{-1}, and atomization energy ($\Delta_a H_0^o$), in kJ mol^{-1}, for the OsC and OsC_2 molecules.

Molecule	State	E^a	IE	EA	$r_{Os\text{-}C}$[b]	$r_{C\text{-}C}$[b]	ν[c]	ZPE	$\Delta_a H_0^o$
OsC	$^3\Sigma^-$	−127.9342	8.54	1.6	1.71		1057	6.32	543.2
OsC^+	$^2\Delta$	−127.6205			1.67		1105	6.61	
OsC^-	$^2\Delta$	−127.9914			1.69		1096	6.56	
OsC_2	$^1A_1$	−165.8902	8.49	0.7[d]	1.75	1.79	195,913,1060[e]	13.0	1050.2
OsC_2^+	$^2A_1$	−165.5778			1.76	1.74	173,829,1030[e]	12.2	
OsC_2^-	$^2A_1$	−165.9159			1.85	1.49	⋯	⋯	

[a] E is in hartree.

[b] The bond distances are in Å.

[c] The vibrational frequencies are in cm^{-1}.

[d] This value does not include ZPE correction.

[e] These frequencies are, in order, bending, symmetric, and antisymmetric stretching vibrational modes.

the mass-to-charge ratios, isotopic abundances, and ionization efficiency curves. At each measurement a movable slit was interposed into the molecular beam to distinguish between ions produced from species in the beam and from residual gases with the same mass-to-charge ratio in the ionization region of the mass spectrometer.

The ionization energies (IE), in eV, were determined by the extrapolated voltage difference method[38] as 8.3±0.5 for OsC, and 8.9±0.5 for OsC_2. The electron energy scale was calibrated with C (11.264 eV).[39] The computed IE values of 8.54 eV for OsC and 8.49 eV for OsC_2 compare well with the experimental values within the given error limits.

The ion current data of the most abundant isotopes of the species pertinent to this investigation are listed in Table IV. The ion intensities measured for the various ions were converted into partial pressures by using the relation $p_i = (K/\sigma_i \gamma_i n_i) I_i T$, where K is the instrumental constant, σ_i, γ_i, n_i, and I_i are the cross section, the multiplier gain, the isotopic abundance, and the ion current of the specific ion, respectively, and T is the temperature. The instrumental constant, K, was determined from the known partial pressures of atomic carbon[40] in the same way as described elsewhere.[41] The cross section for C was taken from Brook *et al.*,[42] the cross section for Os from Mann,[43] and those for OsC and OsC_2 were assumed as 0.75 times the sum of the atomic values. The multiplier gain of C was measured as 7.55 times 10^5. The $\gamma_{Os}/\gamma_{OsC_n}$ $(n=1,2)$ was considered equal to 1, implying cancellation of the mass and molecular effect.

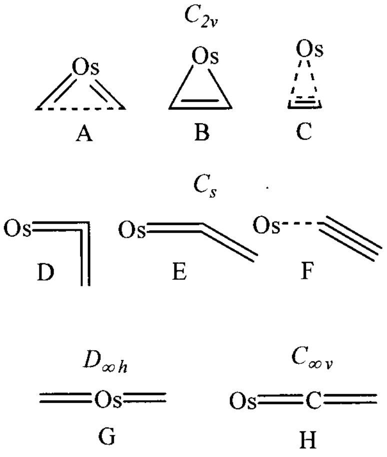

FIG. 1. Structural representation of the eight geometries and their point group investigated at varying levels of theory to determine the global minimum for OsC_2.

During the measurements the instrument has been charged twice with graphite powder, therefore the experimental data have been divided in two sets, series 1 and 2. The resulting values, in bar A^{-1} K^{-1}, of the instrumental constant are 1.41 and 0.891 for series 1 and 2, respectively. The uncertainty of the K values is estimated to be about 20%.

IV. RESULTS AND DISCUSSION

A. Thermal functions

The Gibbs energy functions, $(G_T^o - H_0^o)/T(\mathrm{GEF}_0)$, and the heat content functions, $(H_T^o - H_0^o)(\mathrm{HCF}_0)$, needed in the evaluation of the reaction enthalpies were taken from literature for $C(g)$[40] and $Os(g)$.[44] Those for $OsC(g)$ and $OsC_2(g)$ were calculated according to the statistical thermodynamic procedures, using the harmonic oscillator-rigid rotator approximation.[45] The molecular parameters used for $OsC(g)$ and $OsC_2(g)$, calculated at the CCSD(T) level of theory, are listed in Tables I and III, respectively.

For OsC the first excited state, $^3\Delta$, at 2223 cm^{-1} above the apparent ground state has been included in the calculation of the thermal functions, because it is close in energy to the ground state. Table V lists the thermal functions calculated for OsC and OsC_2.

B. Atomization energies and enthalpies of formation

The following gaseous equilibria,

$$OsC(g) = Os(g) + C(g), \tag{1}$$

$$OsC_2(g) = Os(g) + 2C(g), \tag{2}$$

were evaluated by both the second- and third-law methods, using the standard relationships based on a least-squares analysis of $\ln K_p$ versus $1/T$ plots, and $\Delta_r H_0^o = -RT \ln K_p - T\Delta[(G_T^o - H_0^o)/T]$, respectively. The reaction enthalpies give directly the atomization energies.

TABLE IV. Measured ion currents, in A, over the Ce–Ru–Rh–Os–C system, and third-law values, in kJ mol^{-1}, of the $\Delta_a H_0^\circ$ and $\Delta_f H_{298.15}^\circ$ of OsC and OsC_2.

	Ion intensities				$\Delta_a H_0^\circ$	$\Delta_f H_{298.15}^\circ$	$\Delta_a H_0^\circ$	$\Delta_f H_{298.15}^\circ$
$T(K)$	Os^+	C^+	OsC^+	OsC_2^+	OsC	OsC	OsC_2	OsC_2
Series 1								
2533	$3.10E-12$	$7.80E-10$	$2.80E-12$		608.8	892.2		
2589	$4.80E-12$	$1.25E-09$	$4.20E-12$		606.6	894.4		
2609	$6.30E-12$	$1.95E-09$	$5.49E-12$		601.4	899.6		
2631	$9.00E-12$	$2.69E-09$	$7.80E-12$		599.3	901.7		
2525	$2.60E-12$	$8.10E-10$	$2.10E-12$		599.0	902.0		
2585	$5.10E-12$	$1.47E-09$	$4.65E-12$		603.0	898.0		
2699	$1.29E-11$	$4.10E-09$	$1.13E-11$		605.6	895.4		
2732	$1.50E-11$	$6.60E-09$	$1.46E-11$		604.4	896.6		
2769	$1.68E-11$	$6.20E-09$	$1.59E-11$		613.3	887.7		
2734	$1.29E-11$	$6.00E-09$	$1.08E-11$		603.7	897.3		
Series 2								
2768	$2.13E-11$	$1.24E-08$	$2.10E-11$		608.7	892.3		
2785	$4.57E-11$	$1.83E-08$	$3.80E-11$		599.4	901.6		
2804	$1.86E-10$	$2.19E-08$	$1.64E-10$	$3.25E-12$	600.6	900.4	1158.3	1055.8
2642	$1.88E-11$	$3.55E-09$	$1.82E-11$	$2.10E-13$	608.1	892.9	1161.9	1052.1
2672	$4.00E-11$	$6.40E-09$	$3.30E-11$	$4.35E-13$	598.4	902.6	1148.2	1065.8
2724	$7.80E-11$	$1.05E-08$	$7.05E-11$	$9.90E-13$	600.9	900.1	1151.5	1062.5
2754	$1.14E-10$	$1.50E-08$	$1.07E-10$	$1.78E-12$	600.0	901.0	1152.5	1061.5
2785	$1.48E-10$	$2.10E-08$	$1.41E-10$	$2.81E-12$	599.4	901.6	1154.3	1059.8
2838	$3.24E-10$	$3.52E-08$	$3.30E-10$	$7.20E-12$	600.3	900.7	1155.4	1058.6
					603.2±4.3[a]	897.8±4.3	1154.6±4.5	1059.5±4.5

[a] The error terms are standard deviations.

For OsC the second- and third-law $\Delta_a H_0^\circ$, in kJ mol^{-1}, are 610.5±28.7 and 603.2±4.3, respectively, which are in good agreement. The atomization energy, in kJ mol^{-1}, for OsC is selected as 605.6±14.0, giving the third-law value twice the weight of the second-law value. The computed $\Delta_a H_0^\circ(\mathrm{OsC},g)$ at the CCSD(T) level of theory is 543.2 kJ mol^{-1}, about 10% lower than the experimental result.

For OsC_2 the second-law $\Delta_a H_0^\circ$, in kJ mol^{-1}, is 1154.4 ±72.5, and the third-law value is 1154.6±4.5. The large error of the second-law value is essentially due to the limited number of measurements, and the good agreement is considered, in part, fortuitous. For this reason, the atomization enthalpy, in kJ mol^{-1}, for OsC_2 is selected as the average of the third-law values, 1154.6±18.0. Here, as for the selected value of OsC, the uncertainty is the estimated overall error, calculated as reported by Schmude *et al.*[46] The $\Delta_a H_0^\circ(\mathrm{OsC_2},g)$ calculated at the CCSD(T) level of theory is 1050.2 kJ mol^{-1}, about 9% lower than the experimental value, in line with the result for OsC.

TABLE V. The Gibbs energy functions, $(G_T^\circ - H_0^\circ)/T\,(\mathrm{GEF_0})$, in J K^{-1} mol^{-1}, and the heat content functions, $H_T^\circ - H_0^\circ\,(\mathrm{HCF_0})$, in kJ mol^{-1}, for the OsC and OsC_2 molecules.

		Temperature (K)						
Species		298.15	2200	2400	2600	2800	3000	3200
OsC	$-\mathrm{GEF_0}$	213.3	280.4	283.8	286.9	289.8	292.5	295.0
	$\mathrm{HCF_0}$	8.754	85.18	93.32	101.4	109.4	117.3	125.2
OsC_2	$-\mathrm{GEF_0}$	235.4	327.6	332.2	336.5	340.5	344.2	347.7
	$\mathrm{HCF_0}$	11.62	116.4	127.9	139.4	151.0	162.6	174.2

The corresponding values of $\Delta_a H_{298.15}^\circ$, $\Delta_f H_0^\circ$, and $\Delta_f H_{298.15}^\circ$ for OsC(g) and $OsC_2(g)$ have been derived from the $\Delta_a H_0^\circ$ values, using $\Delta_f H_0^\circ$ and $\Delta_f H_{298.15}^\circ$ of (711.2±0.4) kJ mol^{-1} and (716.7±0.4) kJ mol^{-1} for C(g) from Gurvich *et al.*,[40] and (787.1±3.8) kJ mol^{-1} and (788.3±3.8) kJ mol^{-1} for Os(g) from Hultgren *et al.*,[44] respectively, and the $H_{298.15}^\circ - H_0^\circ$ values from Table V. The enthalpies of formation were calculated employing the relation $\Delta_f H_T^\circ(\mathrm{OsC}_n) = \Delta_f H_T^\circ(\mathrm{Os},g) + n\Delta_f H_T^\circ(\mathrm{C},g) - \Delta_a H_T^\circ(\mathrm{OsC}_n)$, where T is 0 or 298.15 K. The thermodynamic properties of OsC and OsC_2 have been summarized in Table VI.

It is interesting to compare the bond energies of the OsC and OsC_2 molecules with carbides and dicarbides of the same and adjacent transition metals rows.

The dissociation energies (D_0°), in kJ mol^{-1}, of RuC and RhC are 608.8±10.6 (Ref. 26) and 576.0±3.8,[13] respectively, whereas the dissociation energy of PdC is very low compared with RuC and RhC. Only an upper limit for its D_0° value has been obtained, $D_0^\circ \leqslant 430$ kJ mol^{-1}.[15] The low D_0° value of PdC can be explained because of the stability of the closed shell configuration of Pd (4 d^{10}). The bond energy (in kJ mol^{-1}) of OsC compares well to that of RuC, RhC, IrC (627±5),[12] and PtC (606±5).[12] The dicarbides of Ru, Rh,

TABLE VI. Thermodynamic properties for the OsC and OsC_2 molecules. All values are in kJ mol^{-1}.

Molecule	$\Delta_a H_0^\circ$	$\Delta_a H_{298.15}^\circ$	$\Delta_f H_0^\circ$	$\Delta_f H_{298.15}^\circ$
OsC	605.6±14.0	609.6±14.0	892.7±14.0	895.4±14.0
OsC_2	1154.6±18.0	1162.2±18.0	1054.9±18.0	1059.5±18.0

TABLE VII. Comparison between bond strength of gaseous dicarbides and gaseous monoxides of some second- and third-row transition metals. All values are in kJ mol^{-1}.

Metal	Ru	Rh	Os	Ir	Pt
$D_0^o(\mathrm{MO},g)$	524[a]	401[a]	571[b]	410[a]	387[a]
$D_0^o(\mathrm{M\text{-}C_2},g)$	512	426	547	538	539

[a] Reference 50.
[b] Reference 51.

Os, Ir, and Pt have almost the same atomization energies, ranging from (1033±21) kJ mol^{-1} for RhC$_2$[9] to (1155±18) kJ mol^{-1} for OsC$_2$.

We can obtain estimates of the M–C$_2$ bond energies by subtracting the dissociation energy of the C$_2$ molecule, $D_0^o = (607.4 \pm 2.2)$ kJ mol^{-1}, from the atomization enthalpies of the dicarbides. The D_0^o of C$_2$ is obtained using the relationship $D_0^o = 2\Delta_f H_0^o(\mathrm{C},g) - \Delta_f H_0^o(\mathrm{C_2},g)$, where $\Delta_f H_0^o(\mathrm{C},g)$ is from Gurvich *et al.*,[40] and $\Delta_f H_0^o(\mathrm{C_2},g)$ is from Urdahl *et al.*[47] The M–C$_2$ bond energies have almost the same values as the corresponding metal monoxides of Ru, Rh, and Os, indicating a similar stability of the monoxides and the dicarbides. Table VII lists the M–C$_2$ bond energies and the D_0^o values of the corresponding transition metal monoxides. Ir–C$_2$ and Pt–C$_2$ bond energies are higher than the dissociation energies of IrO and PtO, showing a stronger stability of these carbides with respect to the corresponding monoxides. Chupka *et al.*[48] first formulated the hypothesis that the C$_2$ group can be considered to have the functional character of a pseudo-oxygen. More recently Li and Wang[49] carried out a photoelectron spectroscopic investigation, reporting vibrational frequencies and electron affinities of the first row transition metal dicarbide molecules. The comparison of their results with the vibrational frequencies and electron affinity values for the ground state of the corresponding first row transition metal monoxides shows similar trends. This suggested a good correlation in chemical bonding between the group $-\mathrm{C_2}$ and the oxygen atom. It is possible to interpret these results assuming a strong ionic character of the M–C$_2$ bond.

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