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The Atomization Energies of Ternary Cerium–Platinum Metal Monocarbides

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High temperature Knudsen-cell mass spectrometry has been employed to obtain the atomization energies of the first mixed dimetal monocarbides. Knowledge of bond energies of metal to carbon bonds and metal to metal bonds is important in the fields of organometallic chemistry and of catalysis.

There is little known about gaseous dimetal carbides. The molecules M_2C_2 have been reported for aluminum and gallium [1, 2], and a series of dicerium carbides, Ce_2C_n, n = 1–6, have been observed [3]. Mixed dimetal dicarbides have been reported by Stearns and Koh [2] and by Gingerich and associates [4, 5]. Knowledge of dimetal monocarbides is practically nonexistent, except for the molecule Ce_2C_3 and the ion $AuAlC^+$ [2], the latter having been attributed to a fragment product from $AuAlC_2$. The experimental observation of the first mixed dimetal monocarbides and the determination of their atomization energies is presented here.

The mass spectrometer and experimental approach used have been described elsewhere [6]. The Ce–Rh–Ru–Os sample used was intimately mixed with excess graphite and placed into a graphite Knudsen cell. The latter was inserted into a tantalum Knudsen cell. The mixed metal carbide species RhCeC, $RhCeC_2$, RuCeC, $RuCeC_2$ and $RuCeC_3$ were identified by their mass-to-charge ratio and, except for $RuCeC_3$, isotopic abundance distribution and appearance potentials. The values, in eV, for the latter are 6 ± 1, 7.6 ± 0.8, 6.5 ± 1 and 7.5 ± 0.8, respectively, indicating that these ions were produced from their respective parent molecules. A typical set of uncorrected relative ion currents corresponding to the most abundant isotopic composition for rhodium and ruthenium containing species and for Ce^+ measured at 2784 K with 20 eV electrons is given: Ce^+, 1.52×10^{-7}; Rh^+, 2.83×10^{-9}; Ru^+, 3.32×10^{-9}; RhC^+, 3.10×10^{-10}; $RhCe^+$, 3.00×10^{-10}; RuC^+, 3.81×10^{-9}; $RhCeC^+$, $2.4_3 \times 10^{-13}$; $RhCeC_2^+$, $2.9_6 \times 10^{-12}$; $RuCe^+$, 4.37×10^{-10}; $RuCeC^+$, $1.9_4 \times 10^{-12}$; $RuCeC_2^+$, $5.1_4 \times 10^{-12}$ and $RuCeC_3^+$, 3.3×10^{-13}.

The third law reaction enthalpies of the pressure independent reactions involving the mixed mono carbide species are summarized in Table I, together with the derived atomization energies. It was assumed that the effects of relative ionization cross sections and multiplier gains cancel in the equilibrium constant, K_p. The ion currents measured with 20 eV electrons were corrected to correspond to maximum ionization. The estimation of the free energy functions was based on the assumed geometries indicated in Table I. The procedure used was similar to that for $RhMC_2$ [5].

The atomization energies listed in Table I were derived from the measured reaction enthalpies and the following ancillary data: (in kJ mol^{-1}) $\Delta H_{v,o}$[C(graph)], 711.3 ± 2.0 [7]; D_0°(CeRh), 545.6 ± 25 [8]; D_0°(CeRu), 527 ± 25 [9]; D_0°(RhC), 579.5 ± 10 [10]; and D_0°(RuC), 641 ± 13 [9]. Also shown in Table I are the atomization energies calculated from the component diatomic molecules using D_0°(CeC) = 452 ± 29 kJ mol^{-1} [11] and the bond additivity rule.

Comparing the experimental atomization energies with those calculated using the bond additivity rule,

TABLE I. Third-law Enthalpies of Pressure Independent Reactions Involving the Molecules CeRhC and CeRuC and Derived Atomization Energies.

Reaction	No. of Data Sets	Temperature Range (K)	ΔH_0° kJ	Assumed Structure of M	ΔH_0° (M) Exp^a kJ mol^{-1}	ΔH_0° (M) Calcd kJ mol^{-1} ^{b}
CeRh(g) + C(graph) = CeRhC(g)	9	2496–2770	260.2 ± 6.7	Rh–Ce–C	997 ± 40	998 ± 54
			245.2 ± 6.7	Ce–Rh–C	1012 ± 40	1125 ± 35
			225.9 ± 6.7	Rh–C–Ce	1031 ± 40	1031 ± 40
CeRu(g) + C(graph) = CeRuC(g)	4	2770–2800	164.4 ± 1.3	Ru–Ce–C	1074 ± 40	979 ± 54
			149.8 ± 1.3	Ce–Ru–C	1088 ± 40	1168 ± 38
			128.9 ± 1.4	Ru–C–Ce	1109 ± 40	1093 ± 42

^{a}Using ancillary literature data indicated in text. ^{b}Assuming bond additivity and using literature values of diatomic molecules indicated in text.

no clear cut decision can be made and none of the assumed structures can be ruled out. If bent structures would have been considered in addition, somewhat lower experimental dissociation energies would have resulted. The structure Ru–Ce–C appears to be less likely on the basis of an about 100 kJ mol^{-1} higher experimental value as compared with the calculated one. In general the bond strength rather decreases than increases, when an atom forming the bond participates in additional bond formation with a third atom. With this in view the structure Ce–M–C (M = Rh or Ru) remains a possibility.

The most consistent agreement is indicated for the structure M–C–Ce. For this structure, the experimental values also reflect the difference in stability of the diatomic component molecules RuC and RhC, a criterion not met for the M–Ce–C structure with respect to the difference in the stability of CeRu and CeRh. Additional support for the central position of carbon comes from consideration of the only known dimetal monocarbide, Ce_2C, for which the approximate atomization energy is 925 (±60) kJ mol^{-1} [3]. The bond additivity rule yields 904 ± 58 kJ mol^{-1} for the assumed Ce–C–C structure, whereas 690 ± 45 kJ mol^{-1} is obtained for an assumed Ce–Ce–C structure, using $D^{\circ}_{0}(Ce_2) = 238.5 \pm 17$ [12]. Thus the latter structure clearly appears to be ruled out.

The present work demonstrates that the previously unknown gaseous mixed transition metal monocarbides, and by extension, considering the Ce_2C example, dimetal monocarbides are stable compounds with carbon most likely being the central atom. Their stability may be predicted using the additivity rule and experimental or estimated dissociation energies of the corresponding gaseous monocarbides. In view of the high stability of the platinum metal monocarbides (except PdC), carbides containing at least one platinum metal atom appear to be particularly stable. Considering the optimum number of bonds that can be formed, the other metal atom should be d-electron deficient, such as a group III–V transition metal, or an inner transition metal.

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