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Stability of Complex Cerium Carbide Molecules

K. A. GINGERICH, D. L. COCKE and J. E. KINGCADE

Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.

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Transition metals are known to form gaseous carbides of the type MC_n where n is 1 to 4. Dimetal carbides, M_2C_2, have been reported for aluminum and gallium.[1,2] Mixed dimetal carbides involving transition metal atoms have also recently been observed.[2,3] Experimental information concerning new types of gaseous transition metal carbides, MC_n, with n = 5 or 6 and dimetal carbides, M_2C_n, with n from 1 to 6, is reported here for cerium.

Results and Discussion

The Knudsen-cell mass spectrometer and the experimental procedure used have been described previously.[4,5] Insertion of a liquid nitrogen trap in the ion source helped to reduce the background considerably at the very high temperatures used and thus permitted the identification of the new higher polyatomic cerium carbides that were present in very minor concentrations. The cerium carbide molecules were observed over a Ce–Rh–Ru–Os alloy mixed with excess graphite powder which was contained in a graphite Knudsen cell that was enveloped by a tantalum Knudsen cell. Carbon species, C_1 to C_7, and gaseous platinum metal containing carbides and cerium inter-metallic compounds were also observed. A typical set of uncorrected relative ion currents of cerium and carbon containing species measured with 20eV electrons at 2733K is given: C^+, 6.15×10^{-9}; C_2^+, 3.28×10^{-9}; C_3^+, 5.59×10^{-8}; C_4^+, 9.56×10^{-11}; C_5^+, 1.95×10^{-10}; C_6, 1.0×10^{-12}; C_7, 5×10^{-13}; Ce^+, 8.37×10^{-8}; CeC^+, 9.68×10^{-11}; CeC_2, 8.52×10^{-8}; CeC_3, 4.90×10^{-10}; CeC_4, 3.80×10^{-9}; CeC_5, 5.60×10^{-11}; CeC_6, 2.20×10^{-11}; Ce_2C, 4.5×10^{-13}; Ce_2C_2, 9.9×10^{-13}; Ce_2C_3, 1.20×10^{-12}; Ce_2C_4, 2.15×10^{-11}; Ce_2C_5, 3.40×10^{-12}; and Ce_2C_6, 6.9×10^{-13}. Significant fragmentation corrections were only necessary for CeC^+ (approximately 1×10^{-11} after correction).

Information concerning the bond energies of the new carbides was derived from the measured third-law enthaplies for selected pressure independent reactions. The calculation of the necessary free energy functions was based on estimated molecular parameters. Here the molecular structures were chosen so that as many C_2 groups linked to Ce atoms as possible were retained, the remaining links being between single carbon atoms attached to cerium. Linear structures were chosen except for CeC_5 and CeC_6 which were assumed to have trigonal planar geometry with bond angles equal to 120°. The experimental enthalpies given in Table I for reactions involving the molecules CeC_3, CeC_5, and CeC_6 were combined with appropriate literature data to yield the atomization energies listed.

The selected values obtained for the atomization energies, $D^\circ_{a,0}$, in kJ mol^{-1} are: CeC_3, 1802 ± 30; CeC_5, 3077 ± 40 and CeC_6 3782 ± 40, by taking the average of the values derived from the enthalpies of reactions (1) and (2) for CeC_3, of reactions (5) and (6) for CeC_6 and by giving twice the weight to the value derived from the enthalpy of reaction (3) for CeC_5.

The bond additivity concept can be used to discuss the atomization energies and probable geometries of the new CeC_n molecules. Taking the bond energy for the Ce–C_2 bond as 678 kJ mol^{-1} [7] and using the

TABLE I. Third-law Reaction Enthalpies Measured between 2550° and 2800 °K and Derived Atomization Energies of CeC_3, CeC_5, and CeC_6.

Reaction	No. of Data Sets	$\Delta[(G^\circ_T - H^\circ_0)/T]$ T = 2590 K (J K^{-1})	ΔH°_0 3rd Law (kJ)	$D^\circ_{a,0}(M)^a$ (kJ mol^{-1})	M
(1) $Ce(g) + 3\ C(s) = CeC_3(g)$	11	50.1	335 ± 15	1799	CeC_3
(2) $CeC_2(g) + CeC_4(g) = 2CeC_3(g)$	10	62.9	222 ± 15	1805	CeC_3
(3) $Ce(g) + 5\ C(s) = CeC_5(g)$	12	71.9	483 ± 20	3074	CeC_5
(4) $CeC_2(g) + CeC_3(g) = Ce(g) + CeC_5(g)$	5	17.9	– 8 ± 25	3084	CeC_5
(5) $Ce(g) + 6\ C(s) = CeC_6(g)$	7	82.8	490 ± 20	3777	CeC_6
(6) $CeC_2(g) + CeC_4(g) = Ce(g) + CeC_6(g)$	7	43.9	45 ± 20	3788	CeC_6

[a] Using $\Delta H_{v,0}$ [C(graph)] = 711.3 ± 2.0 kJ mol^{-1} (Reference 6), $D^\circ_{a,0}(CeC_2)$ = 1274.0 ± 6.3 kJ mol^{-1} and $D^\circ_{a,0}(CeC_4)$ = 2458 ± 21 kJ mol^{-1} (Reference 7).

literature value for D°_0 (C_2) of 594.1 ± 12.6 kJ mol^{-1} [8] one can construct the bond energy for the Ce–C bond in CeC_3 and CeC_5 as 530 and 533 kJ mol^{-1}, respectively. These values are considerably lower than the value for the Ce–C_2 bond energy, but somewhat higher than the literature value, D°_0(CeC) = 452 ± 29 kJ mol^{-1}.[9] The data obtained in the present investigation thus appear to support the geometries chosen for the CeC_n molecules with respect to their atomic linkage. The pseudo oxygen character of the C_2 group first noted by Chupka *et al.*[1] can also be extended to a molecule with three C_2 groups, such as CeC_6, the average Ce–C_2 bond energy being 667 kJ mol^{-1}, in close agreement with the literature value obtained for CeC_2 and CeC_4.[7]

For the previously unknown Ce_2C_n molecules only approximate atomization energies could be obtained in view of the uncertainties of their molecular structures and the limited experimental data. These approximate $D^\circ_{a,0}$ values in kJ mol^{-1} are: Ce_2C, 925; Ce_2C_2, 1620; Ce_2C_3, 2260; Ce_2C_4, 3000; Ce_2C_5, 3610; and Ce_2C_6, 4260.

Similar polyatomic transition metal carbides with comparable bond energies may be expected especially for lanthanum and thorium, but also for other lanthanide and actinide carbides and for carbides of *d*-block transition metals, especially groups III to VI.

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