Inorganica Chimica Acta, 28 (1978) L171–L172

The Atomization Energies of Gaseous CeOs, CeRu, OsC and OsC_2

KARL A. GINGERICH and DAVID L. COCKE

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

Received April 12, 1978

Platinum metals have been found to form very stable diatomic intermetallic compounds with rare earth metals [1–3].

The present investigation was undertaken to detect intermetallic molecules between cerium and ruthenium and osmium and measure their atomization energies. The dissociation energies of the molecules CeRu and CeOs have recently been predicted [3]. Their experimental determination would permit a test of the proposed method for calculating bond energies of certain diatomic gaseous intermetallic compounds with multiple bonds [3, 4] and at the same time complete the series of diatomic cerium–platinum metal compounds [3, 5].

This investigation could be conveniently combined with a search for gaseous osmium carbides, which had not yet previously been observed. The bond energies of the monocarbides [4, 6–9] and dicarbides [8a, 10] of the other platinum metals, except palladium had previously been measured. Very strong osmium to carbon bonds could be expected from the analogy with the corresponding ruthenium carbides [7, 9], and in case of OsC_2 from the analogy with OsO [10, 11]. Knowledge of the stability of these molecules is expected to aid the understanding of certain canalytic reactions.

The mass spectrometer and experimental approach used have previously been described [5, 12]. A liquid nitrogen cooling trap was inserted into the ion source to minimize background contributions at the very high temperatures necessary for this investigation. The Ce–Rh–Ru–Os sample, that was intimately mixed with excess graphite, was contained in a graphite Knudsen cell that was enveloped by a tantalum cell. Rhodium was present to use its known molecules as standards.

The new molecules CeRu, CeOs, OsC, and OsC_2 were identified by their mass to charge ratio, their isotopic abundance distribution, and their approximate appearance potentials except for CeOs where Ce_2C_4 was overlapping. For the evaluation of the third-law enthalpies of the pressure independent reactions given in Table I it was assumed that the effects of relative ionization cross sections and multiplier gains cancel in the equilibrium constant, K_p. The ion currents were corrected to correspond to maximum ionization. Free energy functions were taken from literature for Rh [13], Ru [13], Os [13], C [14], and RhC [8a]. Those for CeRu, CeOs and OsC were calculated from estimated molecular parameters under similar assumptions as used elsewhere [3, 8b]. The resulting $-(G^\circ_T - H^\circ_0)/T$ in J mol^{-1} K^{-1} at 2600 and 2800 °K, respectively, are 318.0 and 320.7, 325.6 and 328.2, and 273.4 and 276.0. The free energy function change for the reaction OsC_2 + Os = 2 OsC was taken the same as for the corresponding reaction with Rh [8a].

TABLE I. Third Law Reaction Enthalpies for Pressure Independent Reactions Involving the Molecules OsC, RuC, OsC_2, CeRu and CeOs and Derived Atomization Energies.

Reaction	Temp. Range (°K)	No. of Data Sets	ΔH°_0 kJ	D°_0 (M) kJ mol^{-1}	M
RhC(g) + OsC(g) = OsC_2(g) + Rh(g)	2642–2785	5	65.7 ± 1.3	645 ± 13[a]	OsC
RhC(g) + Ru(g) = RuC(g) + Rh(g)	2552–2785	6	61.5 ± 1.3	641 ± 13[a]	RuC
OsC_2(g) + Os(g) = 2OsC(g)	2642–2785	5	−121.3 ± 2.5	1169 ± 21	OsC_2
RuC(g) + Ce(g) = CeRu(g) + C(g)	2576–2770	6	113.8 ± 5.0	527 ± 25[b]	CeRu
OsC(g) + Ce(g) = CeOs + C(g)	2770	2	138.1 ± 0.8	507 ± 33	CeOs
CeOs(g) + Ru(g) = CeRu(g) + Os(g)	2770	2	30.5 ± 0.8	497 ± 33[b]	CeOs

[a] Using D°_0 (RhC) = 579.5 ± 10.5 kJ mol^{-1} (Ref. 8). [b] Using the respective D°_0 values for OsC, RuC and CeRu from this investigation.

The error terms shown for the reaction enthalpies in Table I correspond to standard deviations, and in case of the reactions with CeOs, to the deviation from the mean value. The reaction enthalpies were combined with the appropriate D°_0 values of other reaction participants, to yield the dissociation or atomization energy of the corresponding molecule specified. In case of OsC_2 the value $D^\circ_0(C_2) = 591.1 \pm 12.6$ kJ mol^{-1} [14] was used in addition. Here the error terms in Table I take the estimated experimental errors into account, as well as the errors introduced from the assumptions used in arriving at the equilibrium constants and the free energy function changes.

The dissociation energies, D°_0, of CeRu (527 ± 25 kJ mol^{-1}) and CeOs (503 ± 33 kJ mol^{-1}) agree with the respective values of 544 and 536 kJ mol^{-1} calculated previously [3] assuming a triple bond, but appear to be slightly lower. This gives further support to the applicability of the proposed method for calculating dissociation energies of diatomic rare earth–platinum metal intermetallic compounds. The fact that the dissociation energies of CeRu and CeOs are not larger than the calculated values may be taken as indication that the 4*f*-electron of cerium does not appreciably participate towards formation of a possible quadruple bond.

The osmium monocarbide molecule is as or slightly more stable than gaseous RuC (See Table I) and thus, with RuC, the most stable of any gaseous diatomic metal carbide. The osmium dicarbide is the most stable platinum metal dicarbide.

With $D^\circ_0(C_2)$ [14], the energy of the Os–C_2 bond is obtained as 575 ± 29 kJ mol^{-1}. This value is consistent with the upper value of 590 kJ mol^{-1} for the dissociation energy of OsO [11], and thus with the applicability of pseudo-oxide concept to transition metal dicarbides, including the platinum metal dicarbides [10].

Acknowledgement

The support by the Robert A. Welch Foundation is gratefully acknowledged.

References

1 K. A. Gingerich, *High Temp. Science, 3,* 415 (1971).
2 D. L. Cocke, K. A. Gingerich and J. Kordis, *High Temp. Science, 5,* 474 (1973).
3 K. A. Gingerich, *J. Chem. Soc. Faraday Trans. II, 70,* 471 (1974).
4 K. A. Gingerich, *Chem. Phys. Letters, 23,* 270 (1973).
5 D. L. Cocke and K. A. Gingerich, *J. Phys. Chem., 76,* 2332 (1972); Erratum, 4042.
6 A. Vander Auwera-Mahieu and J. Drowart, *Chem. Phys. Letters, 1,* 311 (1967).
7 N. S. McIntyre, A Vander Auwera-Mahieu and J. Drowart, *Trans. Faraday Soc., 64,* 3006 (1968).
8 D. L. Cocke and K. A. Gingerich, *J. Chem. Phys., 57,* 3654 (1972); *60,* 1958 (1974).
9 K. A. Gingerich, *Chem. Phys. Letters, 25,* 523 (1974).
10 K. A. Gingerich, *Chem. Commun.,* 199 (1974).
11 L. Brewer and G. M. Rosenblatt, *Adv. High Temp. Chem., 2,* 1 (1969).
12 J. Drowart and P. Goldfinger, *Angew. Chem., 79,* 589 (1967).
13 R. Hultgren, R. L. Orr and K. K. Kelly, *Supplement to Selected Values of Thermodynamics Properties of Metals and Alloys,* University of California, Berkeley (1972).
14 "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Michigan (1965).