Mass Spectrometric Observation and Stability of Gaseous RuC_2, PtC_2, and IrC_2

By KARL A. GINGERICH

(*Department of Chemistry, Texas A&M University, College Station, Texas* 77843)

Summary. The gaseous molecules RuC_2, PtC_2, and IrC_2 have been observed in a high-temperature mass spectrometer and their atomization energies, $\Delta H^\circ_{\mathrm{atm,0}}$, have been determined as $1119{\cdot}0 \pm 38$, $1084{\cdot}1 \pm 38$ and $\leqslant 1088{\cdot}3 \pm 42$ kJ mol^{-1}.

PLATINUM metals have been found to form very stable monocarbides. Spectroscopic studies have been reported for the molecules RhC and PtC.[1] Dissociation energies for these two molecules and RuC and IrC have been obtained by Drowart and his collaborators[2,3] who failed, however, to observe the corresponding dicarbides, MC_2. The only platinum metal dicarbide observed so far is RhC_2.[4] For this molecule the pseudo-oxide character noted for other transition-metal dicarbides[5] was indicated.

We have attempted to detect the dicarbides of Pt, Ir, and Ru and to measure their atomization energies. Knowledge of the stability of these molecules should help to understand the action of platinum metal catalysts in reactions involving carbon-containing molecules.

The mass spectrometer and experimental approach used were similar to those described.[4,6] The samples were contained in a graphite Knudsen cell enveloped by a tantalum cell. The molecules PtC_2 and IrC_2 have been measured at 2710 and 2724 K above the residue of a Ce–Th–Zr–Rh–Pt–Ir system. Ruthenium dicarbide was observed over a Ru–Os sample at temperatures between 2635 and 2745 K. The platinum metal dicarbides were identified by their mass to charge ratio and for RuC_2 and PtC_2 by their isotopic abundance distribution and their approximate appearance potentials. Because of the comparatively large background contribution at these high temperatures the effective sensitivity and precision of measurement were lowered. A typical set of relative ion currents (mass nos. in parentheses) involving platinum and iridium dicarbides at 2710 K is: Pt^+ (194), 17,100; Ir^+ (193), 615; PtC^+ (206), 1650; IrC^+ (205), 345; PtC_2^+ (218), 2·2; PtC_2^+ (219), 2·3; PtC_2^+ (220), 1·7; IrC_2^+ (217), 0·6; C^+, 34,310; C_2^+, 17,250. For the ruthenium–carbon system a typical ratio of ion currents as measured at 2635 K for RuC_2^+–RuC^+–Ru^+ is 1:350:930.

For the evaluation of the third-law enthalpies[6] (Table) of reaction (1) it was assumed that the effects of relative

$$MC_2(g) + M(g) = 2MC(g) \qquad (1)$$

ionization cross sections and multiplier gains cancel in the equilibrium constant, K_p. The free-energy function change of reaction (1) was taken to be the same as for the corresponding reaction with M = Rh.[4]

Combination of the reaction enthalpies with the appropriate dissociation energies for the monocarbides: D_0^0 (PtC) = 604·5 ± 10·5 kJ mol^{-1};[7] D_0^0 (IrC) = 623·0 ± 10·5 kJ mol^{-1};[7] D_0^0 (RuC) = 631·7 ± 12·6 kJ mol^{-1},[3] yields the atomization energies (Table). Assuming the asymmetric structure MCC for the dicarbides[5] and subtracting the dissociation energy D_0^0 (C_2) = 594 ± 13 kJ mol^{-1} [8] from these atomization energies, the M–C_2 bond energies are obtained (Table). The error limits given in the Table for the D_0^0 (MC_2) and D_0^0 (M–C_2) values take into account the experimental errors, the errors introduced from the assumptions used in arriving at the equilibrium constants and the free-energy function changes and the uncertainties in ancillary literature values used. Since the $^{193}IrC_2^+$ ion current was measured near the detection limit, the derived D_0^0 (Ir–C_2) values may possibly be upper limits.

Table. Third-law reaction enthalpies for MC_2 + M = 2MC and derived atomization energies, D_0^0 (MC_2) and D_0^0 (M–C_2) bond energies of platinum metal dicarbides

Reaction	T/K	log K_p	$-\Delta H$/kJ	D_0^0 (MC_2) /kJ mol^{-1}	D_0^0 (M–C_2) /kJ mol^{-1}	MC_2	D_0^0 (MO) /kJ mol^{-1}	MO
PtC_2 + Pt = 2PtC	2710	1·860	127·2	1084·1 ± 38	490 ± 42	PtC_2	343 ± 33	PtO
	2724	1·751	122·6					
IrC_2 + Ir = 2IrC	2710	2·501	161·0	⩽1088·3 ± 42	⩽494 ± 42	IrC_2	⩽389	IrO
	2724	2·426	157·7					
RuC_2 + Ru = 2RuC	2635	2·151	138·1	1119·0 ± 38	525·5 ± 38	RuC_2	477 ± 63	RuO
	2735	2·232	148·5					
	2745	2·154	157·7					
				1033·4 ± 21	439·3 ± 21	RhC_2	372 ± 63	RhO

The dissociation energies of the corresponding platinum metal monoxides[9] and the results for RhC_2[4] are also given in the Table for comparison with the M–C_2 bond energies. The D_0^0 (M–C_2) values are consistently somewhat larger than the corresponding D_0^0 (MO) values, but only in case of PtC_2 (and possibly IrC_2) are they larger considering the combined error limits. For dicarbides of more electropositive transition metals[5] the M–C_2 bond energies are usually slightly lower than the corresponding MO dissociation energies. The rather large uncertainties in the knowledge of the dissociation energies of most platinum metal monoxides does not at present permit a more detailed test of the pseudo-oxide concept for the platinum metal dicarbides, but it applies at least in a qualitative sense. Thus the outstanding feature for the gaseous platinum metal carbides as compared with other transition-metal carbides is not the low stability of the dicarbides (even these appear to be slightly more stable than expected) but the very high stability of the monocarbides (except PdC), owing to multiple bond formation.

This work was supported by the National Science Foundation.

(*Received*, 19*th November* 1973; *Com.* 1589.)

---

[1] H. Neuhaus, R. Scullman, and B. Yttermo, *Z. Naturforsch.*, 1965, **20a**, 162; A. Lagerqvist, H. Neuhaus, and R. Scullman, *ibid.* p. 751; A. Lagerqvist and R. Scullman, *Arkiv Fysik*, 1966, **32**, 479; R. Scullman and B. Yttermo, *ibid.*, 1966, **33**, 231; O. Appelblad R. F. Barrow, and R. Scullman, *Proc. Phys. Soc.*, 1967, **91**, 260; B. Kaving and R. Scullman, *J. Mol. Spectroscopy*, 1969, **32**, 475; J. M. Brom, Jun., W. R. M. Graham, and W. Weltner, Jun., *J. Chem. Phys.*, 1972, **57**, 4116.

[2] A. Vander Auwera-Mahieu and J. Drowart, *Chem. Phys. Letters*, 1967, **1**, 311.

[3] N. S. McIntyre, A. Vander Auwera-Mahieu, and J. Drowart, *Trans. Faraday Soc.*, 1968, **64**, 3006.

[4] D. L. Cocke and K. A. Gingerich, *J. Chem. Phys.*, 1972, **57**, 3654.

[5] G. DeMaria, in 'Chemical and Mechanical Behaviour of Inorganic Materials,' eds., A. W. Searcy, D. V. Ragone, and U. Colombo, Wiley-Interscience, New York, 1970, pp. 81—105; C. A. Stearns and F. J. Kohl, *Adv. Mass Spectrometry*, 1971, **5**, 371.

[6] J. Drowart and P. Goldfinger, *Angew. Chem.*, 1967, **79**, 589; *Angew. Chem. Internat. Edn.*, 1967, **6**, 581.

[7] K. A. Gingerich, *Chem. Phys. Letters*, 1973, **23**, 270.

[8] 'JANAF Thermochemical Tables,' Dow Chemical Co., Midland, Michigan, 1965.

[9] L. Brewer and G. M. Rosenblatt in *Adv. High Temperature Chem.*, 1969, **2**,1.