Thermodynamic Confirmation for the High Stability of Gaseous TiRh as Predicted by the Brewer–Engel Metallic Theory and the Dissociation Energy of Diatomic Rhodium

By K. A. Gingerich* and D. L. Cocke†
(*Department of Chemistry, Texas A. & M. University, College Station, Texas* 77843)

Summary The dissociation energies of the molecules TiRh and Rh_2 have been determined as 88·9 ± 5 kcal mol^{-1} and 65·5 ± 6 kcal mol^{-1}, respectively, and the former value is interpreted in terms of the Brewer-Engel metallic theory.

Recent reviews indicate considerable interest in strong metal to metal bonds between ligand free metal atoms[1] and between pairs of metal atoms in complex compounds.[2] Unusually strong metal to metal bonding has also been predicted by the Brewer–Engel metallic theory between Group IV transition metals and platinum metals,[3,4] and confirmed in several instances.[3a,5,6] Mass spectrometric evidence for a similar high stability of the corresponding gaseous intermetallic compounds as predicted by the Brewer-Engel theory[7] has recently been presented.[8] According to these semiquantitative spark-source experiments, the molecule TiRh appeared to be particularly suitable for a quantitative test of the theory, involving direct bond energy measurement. For the assessment of the relative merits (in the case of TiRh) of the Brewer-Engel theory and the Pauling model of a polar single bond[9] a knowledge of the dissociation energy of diatomic rhodium is necessary.

We could identify the molecules TiRh and Rh_2, with a mass spectrometer, in a titanium-rich Ti–Rh alloy contained in a graphite lined tantalum Kundsen cell. The principles of the method and the experimental procedure have been described elsewhere.[10,11]

The reactions (1) and (2) were studied.

$$RhC(g) + Ti(g) = TiRh(g) + C(g) \qquad (1)$$

$$RhC(g) + Rh(g) = Rh_2(g) + C(g) \qquad (2)$$

The dissociation energy, $D_0{}^0$(TiRh), was obtained from the measured reaction enthalpy, $\Delta H_0{}^0$ (1) (Table) according to the relation

$$\begin{aligned}\Delta H_0{}^0 &= -RT \ln K_p - T\Delta[(G_T{}^0 - H_0{}^0)/T] \\ &= D_0{}^0(\mathrm{RhC}) - D_0{}^0(\mathrm{TiRh})\end{aligned}$$

The equilibrium constant, K_p (Table) was directly obtained as the product of the relative ion intensities, $TiRh^+$, C^+, RhC^+, and Ti^+, after correcting the latter to correspond to maximum ionization.[11] Here the effects of the relative ionization cross sections and electron multiplier gains were assumed to cancel. Reaction (2) was treated similarly. In view of the high symmetry of the two reactions the cross section and multiplier assumption is estimated to introduce an error of less than 30% in K_p.

Table

Enthalpy change for the exchange reaction (1)

Temp. (K)	$-\log K^a$	$-\Delta[(G_T{}^0 - H_0{}^0)/T]$ (cal K^{-1})	$\Delta H_0{}^0$ (kcal)
2215	3·874	3·94	48·0
2309	3·836	3·87	49·5
2282	3·992	3·87	50·5
2342	3·749	3·84	49·1
2372	3·734	3·83	49·6
2403	3·746	3·80	50·3
2433	3·705	3·79	50·5
			49·6

[a] Typical relative ion currents (at 2342 K) are: Ti^+, 6·96 × 10^{-10}; C^+, 1·82 × 10^{-11}; RhC^+, 2·11 × 10^{-11}, and $TiRh^+$, 1·44 × 10^{-12}.

The numerical values for the free energy functions, $-(G_T{}^0 - H_0{}^0)/T$ were taken from literature for C, Ti, Rh,[12] and RhC.[13] Those for Rh_2 and TiRh were calculated using the harmonic oscillator rigid rotator approximation with the respective estimated values for the vibration frequency, ω_e = 267 and 408 cm^{-1}, the interatomic distance, r_e = 2·28 and 2·325 Å, and the electronic contribution 3 and 5 cal K^{-1}.

For reaction (2) five values of $\Delta H_0{}^0$ were measured between 2461 and 2608 K with a mean of −73·0 ± 5·0 kcal. Combined with $D_0{}^0$(RhC) = 138·5 ± 1·5[13] kcal mol^{-1}, the dissociation energy, $D_0{}^0(Rh_2)$ = 65·5 ± 6 kcal mol^{-1}, is obtained. This value represents the highest bond energy so far measured between two like metal atoms.[1]

For gaseous TiRh we obtain from $\Delta H_0{}^0(1)$ = 49·6 ± 4 kcal (Table) and the known value for $D_0{}^0$(RhC) a dissociation energy, $D_0{}^0$ = 88·9 ± 5 kcal mol^{-1}. This value very much exceeds the upper value of 60 kcal mol^{-1} calculated after the Pauling model of a polar bond$_0$ using D(Rh–Rh) = 65·5 kcal mol^{-1} and D(Ti–Ti) = 32 kcal mol^{-1}[1] as "covalent single bond energies" and confirms the strong multiple bonding predicted by the Brewer–Engel theory. Therefore, we can expect similarly strong bonding in gaseous intermetallic compounds between other combinations of a Group IV transition metal and a platinum group metal.

This work was sponsored by the National Science Foundation and by the Phillips Petroleum Company through a Fellowship to D. L. Cocke.

(*Received*, 21*st February* 1972; *Com.* 321.)

---

† Work performed as part of the Ph.D. degree requirement by D. L. Cocke.

[1] K. A. Gingerich, *J. Cryst. Growth*, 1971, **9**, 31.

[2] F. A. Cotton, *Accounts Chem. Res.*, 1969, **2**, 240.

[3] L. Brewer, *Acta Metallurgica*, 1967, **15**, 555; Science, 1968, **161**, 115.

[4] W. Hume-Rothery, *Progr. Materials Sci.*, 1967, **13**, (No. 5), 248.

[5] P. R. Wengert, Ph.D. Thesis, Lawrence Radiation Laboratory Report (UCRL-18723), University of California, April 1969.

[6] R. S. Carbonara and G. D. Blue, *High Temp. Science*, 1971, **3**, 225.

[7] L. Brewer, personal communication.

[8] K. A. Gingerich and R. D. Grigsby, *Metallurgical Trans.*, 1971, **2**, 917.

[9] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960, Ch. 3.

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

[11] D. L. Cocke and K. A. Gingerich, *J. Phys. Chem.*, 1971, **75**, 3264.

[12] R. Hultgren, R. L. Orr, and K. K. Kelly, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys", University of California, Berkeley, California, 1966, (Ti), 1971 (Rh), 1965 (C).

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