The Dissociation Energies of Rhodium Phosphide and Platinum Phosphide

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The identification of stable monoborides [1, 2], monocarbides [2, 3], and monosilicides [1, 4] of several transition elements suggested the existence of phosphides of similar stability. This paper reports on the identification of the molecule RhP and its dissociation energy as well as on an upper limit for the dissociation energy of the molecule PtP.

Experimental

The mass spectrometer, the general experimental technique, and the methods for obtaining thermodynamic data have been described previously [5, 6]. In the present investigation, the Knudsen cells were made of high density graphite and contained rhodium or platinum metal and gadolinium phosphide. The channel orifices had 0.8 and 1.0 mm diameter and 1 mm length.

Results

The identification of the neutral species effusing from the Knudsen cell was based, after their ionization by electron impact, on the measurement of the mass, the isotopic ratio, the intensity profile in the molecular beam and, where possible, the appearance potentials.

In addition to the species already observed in the C—P—Gd [7], the Rh—C [3], and the Pt—C [3] systems, the molecule RhP was observed. At 2500 K, for ionizing electrons of 20 eV, the relative intensities of P^+ (corrected for a 7% contribution due to fragmentation of P_2), P_2^+, Rh^+, RhP^+ were about $5 \cdot 10^4/10^5/7 \cdot 10^2/1$ in the system C—P—Gd—Rh. In the case of Pt, at 2267 K the corresponding intensities were $8 \cdot 10^3/3 \cdot 10^4/6/1$. Due to more pronounced interaction of Pt than of Rh with the C—P—Gd system, an appreciable vaporization of phosphorus occured at 2000—2200 K, thereby explaining the less favorable detection limit for the PtP molecule.

The dissociation energies were determined using the reaction

$$MP(g) + P(g) \rightarrow M(g) + P_2(g). \qquad (1)$$

The equilibrium constants K_p were calculated from the relative ion intensities assuming the product of the ionization cross sections and of the secondary electron multiplier gains to be unity. A possible deviation of 50% from this assumption is taken into account in the evaluation of the final uncertainty.

For the calculation of the reaction enthalpy by the third law method, the numeric values of the free energy functions were taken from the literature [8] for $P_{(g)}$, $P_{2(g)}$, $Rh_{(g)}$ and $Pt_{(g)}$, while those for RhP and PtP were calculated with the statistical mechanical formulae for the harmonic oscillator and rigid rotator. The interatomic distances,

$$r(\mathrm{RhP}) = 2.02\ \text{Å} \quad \text{and} \quad r(\mathrm{PtP}) = 2.06\ \text{Å},$$

were evaluated by comparison with those of RhC, RuO, PtC and PtO [9]. The vibration frequencies,

$$\omega(\mathrm{RhP}) = \omega(\mathrm{PtP}) = 600\ \mathrm{cm}^{-1},$$

were similarly estimated.

The electronic ground states, $^1\Sigma$ for RhP and $^2\Pi$ for PtP, were choosen by analogy with those of the isoelectronic molecules PtC [9] and AuSi [9] respectively; the multiplet separation, 1071 cm^{-1}, in the latter molecule was also retained. The numeric values of the free energy functions $-(G_T^0 - H_0^0)/T$ at 2200 and 2500 K are 65.84 and 66.93 for RhP and 69.91 and 71.07 cal/deg. mole for PtP.

Table 1. Enthalpy change for the reactions $MP(g) + P(g) \rightarrow M(g) + P_2(g)$.

Exp. No.	T K	log K_p	$-\Delta(G_T^0 - H_0^0)/T$ cal/deg. mole	ΔH_0^0 kcal/mole
Rh				
3807	2451	3.27	1.12	−33.6
	2502	3.11	1.14	−32.4
	2502	3.11	1.14	−32.4
3808	2472	3.15	1.13	−32.5
	2498	3.15	1.14	−32.8
	2472	3.14	1.13	−32.4
	2472	3.19	1.13	−33.0
	4272	3.09	1.13	−31.8
	2518	3.06	1.14	−32.0
			Average:	-32.5 ± 0.6
Pt				
3806	2267	$\geqq 1.35$	1.05	$\leqq -16.4$

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The dissociation energies of the molecules RhP and PtP derived from the enthalpy differences (Table 1) associated with reaction (1) and $D_0^0(P_2) = 116.0 \pm 1$ kcal/mole [10], are

$$D_0^0(\mathrm{RhP}) = 83.5 \pm 4 \text{ kcal/mole}$$

and $$D_0^0(\mathrm{PtP}) \leqq 99.6 \pm 4 \text{ kcal/mole.}$$

The trends in dissociation energies from $D_0^0(\mathrm{RhSi}) = 94 \pm 4$ [1] to $D_0^0(\mathrm{RhP}) = 84 \pm 4$ and from $D_0^0(\mathrm{PtSi}) = 119 \pm 4$ [1] to $D_0^0(\mathrm{PtP}) \leqq 100 \pm 4$ are similar, respectively, to those from $D_0^0(\mathrm{RhSi}) = 94 \pm 4$ to $D_0^0(\mathrm{PdSi}) = 74 \pm 3$ [1] and from $D_0^0(\mathrm{PtSi}) = 119 \pm 4$ to $D_0^0(\mathrm{AuSi}) = 74 \pm 3$ [1] kcal/mole, as expected for isoelectronic molecules. These trends are also similar to those suggested [2] for the nitrides of these metals. They tend thereby to confirm the molecular orbital scheme [2, 11] proposed for this type of molecules, based on the filling of bonding molecular orbitals correlating with the d shell of the metal, followed by σ and π orbitals correlating with the non-metal, the π orbital being occupied for AuSi and presumably PtP, but not for RhSi, RhP or PtSi. It is however delicate to deduce the bonding characteristics of the latter orbital from the measured dissociation energies since the marked increase in ionization potential from IP(Si) = 8.151 to IP(P) = 10.486 eV [12] probably determines to a large extent the variation of the bond strength from RhSi to RhP and from PtSi to PtP.

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Anisotropie der ^{195}Pt-KMR-Verschiebungen kristalliner Tetracyanoplatinate(II) und des $K_2[Pt(CN)_4]Br_{0,3} \cdot 2{,}3\ H_2O$

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The principle values of the ^{195}Pt-shift tensor in a series of tetracyanoplatinates(II) crystallizing in columnar stacks do not depend essentially on the platinum-platinum distance. Knight-shifts and line broadening of ^{195}Pt resonances in $K_2[Pt(CN)_4]Br_{0,3} \cdot 2.3\ H_2O$ prove the existence of a one-dimensional metallic state.

Im Rahmen von Untersuchungen an quadratisch koordinierten Übergangsmetallkomplexen mit sogenannter Kolumnarstruktur wurde kürzlich die Anisotropie der ^{195}Pt-KMR-Verschiebungen von kristallinen Chloro-, Oxalato-, Ammin- und Cyano-Komplexen des Platin(II) bestimmt [1, 2]. Dabei zeigte sich, daß die $\sigma_{\|}$-Komponente des Verschiebungstensors mit zunehmender Stärke der äquatorialen Liganden bei deutlich höherem Magnetfeld auftritt, während die $\sigma_{\perp}$-Komponente nur wenig von dem Charakter dieser Liganden abhängt.

Um den Einfluß einer möglichen Wechselwirkung zwischen den Zentralmetallionen benachbarter Komplexeinheiten einer Kette auf die chemische Verschiebung zu ermitteln, wurden die ^{195}Pt-Messungen an einer Reihe von Tetracyanoplatinaten(II) fortgeführt (Tab. 1). Bei diesen Verbindungen variiert der Pt-Pt-Abstand zwischen 3,09 und 3,60 Å [3]. Die bemerkenswerte Vertiefung der Farbe mit abnehmender Distanz [4] zwischen den Platinionen wurde schon früher einer merklichen Überlappung der Metall-d-Orbitale entlang der Kette zugeschrieben [5, 6]. Wie aus den in Tab. 1 angeführten Ergebnissen hervorgeht, verschiebt sich die $\sigma_{\perp}$-Komponente mit abnehmendem Pt—Pt-Abstand nur unwesentlich nach tieferem Magnetfeld, d. h. die elektronische Umgebung eines Platinkerns ändert sich dabei relativ wenig.

Kürzere Pt—Pt-Abstände werden möglich durch Verringerung der Elektronendichte zwischen den Komplexebenen einer Säule durch partielle Oxidation. So entsteht z. B. aus Kaliumtetracyanoplatinat(II) durch Behandeln mit Brom [7] die Verbindung $K_2[Pt(CN)_4]Br_{0,3} \cdot 2{,}3\ H_2O$, in der dem Zentralmetallion eine mittlere Oxidationszahl von 2,3 zukommt [8]. Der Pt—Pt-Abstand erreicht mit 2,887 Å [8] fast den Wert von metallischem Platin (2,78 Å) [9]. Durch wirksame Überlappung der hier nur teilweise besetzten d_{z^2}-Bahnfunktionen entlang der Platinkette ist mit der Ausbildung eines Leitungsbandes zu rechnen. Eine metallische Leitfähigkeit entlang der kristallographischen c-Achse ist allerdings wegen der unvermeidlichen Kristallbaufehler nicht zu erwarten und auch bislang nicht beobachtet wor-

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