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Mass Spectrometric Study of the Stabilities of the Gaseous Molecules Pt_2 and PtY

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The diatomic metallic molecules Pt_2 and PtY have been observed in the gas phase above a platinum-yttrium-graphite system by Knudsen cell mass spectrometry. Thermodynamic evaluation of the gaseous reaction equilibria involving these species yielded the following dissociation energies: $D_0°(Pt_2) = 358 \pm 15$ kJ mol^{-1} or 84.5 ± 3.6 kcal mol^{-1}; $D_0°(PtY) = 470 \pm 12$ kJ mol^{-1} or 112.4 ± 2.9 kcal mol^{-1}. These values are concordant with the trends in the bond energies of known transition-metal dimers and with the bond energies of previously known diatomic intermetallic molecules containing platinum. The results are discussed in relation to the various empirical models for interpreting the dissociation energies of diatomic metal molecules.

Introduction

The properties of small ligand-free metal clusters are of fundamental significance for an understanding of phenomena such as catalysis by dispersed metals, nucleation, crystal growth, and cluster compound chemistry. From the thermodynamic viewpoint, the principal property of interest in these physicochemical processes is the strength of the metal to metal bond as a function of the cluster size. While thermodynamic measurements on larger clusters are presently not feasible, the dissociation energies of diatomic molecular metals can be determined with relative ease, primarily by the technique of Knudsen effusion at high temperatures combined with mass spectrometry. The experimentally determined dissociation energies provide a basis for improving and developing empirical or semiempirical models for such molecules and, hence, allow an insight into their electronic and chemical properties. The information derived would be valuable as a starting point for the treatment of larger clusters.

As part of a continuing program concerned with the investigation of the thermochemistry of gaseous homo- and heteronuclear molecular metals, we have mass spectrometrically observed two platinum-containing molecules, $Pt_2(g)$ and PtY(g), and determined their dissociation energies. Platinum is one of the technologically more important metals.

It is now well-known that the platinum group metals, which have nearly filled d orbitals, form particularly stable diatomic molecules with early transition metals, which are d-electron deficient. The unusually high dissociation energies for such gaseous molecules were first suggested by Brewer[1] on the basis of the observed extraordinary stabilities of the corresponding metal alloys.[2] The predictions by the Brewer-Engel theory[3] were subsequently confirmed experimentally.[4,5] The existence of the gaseous intermetallic compounds of high stability was first experimentally proven by Gingerich and Grigsby[6] through spark source mass spectrometric studies. Since then a large number of such molecules have been observed and their dissociation energies measured.[7-12] No theoretical treatments which quantitatively account for the dissociation energy of transition-metal molecules have been developed as yet; however, it is generally recognized that bonding in these molecules involves multiple-bond formation between one or more d electrons from each atom. In recent years, several empirical models have been developed which attempt to estimate or predict dissociation energies of gaseous intermetallic compounds. A empirical valence-bond approach developed by Gingerich has been remarkably successful when applied to the aforementioned class of platinum-metal (Ru, Rh, Pd, Os, Ir, Pt) intermetallic compounds.[13] However, in the case of the intermetallic compounds of platinum itself, the experimental stabilities are found to be higher than those calculated by the model for lack of a suitable valence state for the formation of triple bonds.[13] Recently, Miedema and Gingerich[14] have proposed an empirical model which relates the dissociation energy of the dimer, the heat of vaporization, and the surface energy of a pure solid metal and thereby have estimated the dissociation energies of the metal dimers for which no experimental information is available. The model has been extended,[15] by the same workers, to estimate the dissociation energies of diatomic intermetallic molecules from the differences in the electronegativities and the electron density at the boundary of a solid Wigner-Seitz atomic cell.

The aim of the present investigation, thus, was to observe and measure the dissociation energies of $Pt_2(g)$ and PtY(g) and thereby to test the applicability of the various empirical models for bond energies of diatomic metal molecules.

Experimental Section

The instrument, a Nuclide (12-90-HT) magnetic focusing mass spectrometer, and the experimental technique have been described previously.[16,17] The Knudsen cell was made of tantalum and lined with a graphite crucible, both with knife-edge orifices of 1 mm diameter. A charge consisting of platinum (wire, 217 mg), yttrium (chips, 11 mg), and graphite (powder, 50 mg) was placed inside the cell together with a small amount of gold (wire, 17 mg) for instrument sensitivity determination purposes. The graphite powder had the purpose to assure unit activity of carbon in the condensed system, so that graphite could be used as a reaction participant in the evaluation of the gaseous carbides that were observed. Temperatures inside the Kundsen cell were measured with a Leeds and Northrup optical pyrometer by sighting at a black-body hole in the bottom of the cell. The pyrometer had been calibrated in situ by observing the melting point of an NBS reference sample of gold in a graphite Knudsen cell. The calibration was extended to the higher range of temperatures of the actual experimental measurements through the use of neutral

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Table I. Experimental and Estimated (in Parentheses) Parameters and the Pressure Constants for Calculating Absolute Partial Pressures

ion	*m/e*	appearance potential, eV	ionization cross section σ_i, Å^2	multiplier gain ν_i ($\times 10^4$)	intensity correction factor E_i	isotopic abundance n_i	pressure const k_i, atm A^{-1} K^{-1}
Au	197	9.22[a]	5.85	5.83	1.18	1.000	4.12
Pt	195	8.6 ± 0.5	6.60	6.39	1.25	0.338	10.44
Pt_2	390	7.3 ± 2.0	(9.9)	6.39[b]	1.25[b]	0.250	9.41
Y	89	7.0 ± 0.5	11.91	9.70	1.09	1.000	1.12
PtY	284	6.3 ± 2.0	(13.88)	(8.05)	1.14	0.338	3.61

[a] Used as reference for calibrating the electron energy scale.[18] [b] Value assumed to be the same as that for Pt.

Table II. Calculated Values of the Free-Energy Functions (in J mol^{-1} K^{-1}) and Heat Content Functions (kJ mol^{-1}) for Gaseous PtY and Pt_2

	PtY		Pt_2	
temp, K	$-(G_T° - H_0°)/T$	$H_T° - H_0°$	$-(G_T° - H_0°)/T$	$H_T° - H_0°$
298.15	238.29	9.987	232.49	9.919
2400	312.54	88.388	306.52	88.757
2500	314.05	92.128	308.03	92.643
2600	315.49	95.868	309.49	96.557
2700	316.88	99.608	310.89	100.502
2800	318.23	103.348	312.24	104.478

density filters of appropriate thickness. Thus temperatures could be measured with an accuracy of ±10 K at up to 3000 K.

The effusive molecular beam was ionized with a 19-eV electron beam at a total emission of 0.5 mA and a trap current of 50 μA. The ions were accelerated through a potential of 4.5 kV and detected with a 20-stage Cu–Be electron multiplier whose entrance shield was maintained at about −2000 V. The current gain of the electron multiplier was measured by the use of a Faraday cup collector. The ionic species detected were identified by their mass-to-charge ratio and isotopic abundance, and the origin of their neutral precursors from the Knudsen cell was ascertained with a molecular beam shutter located between the cell and the ion source.

Results

The ions Y^+, Pt^+, PtY^+, and Pt_2^+ were detected, and their intensities were measured in the temperature range of 2259–2736 K. Their appearance potentials determined by the linear extrapolation method, relative to that of Au^+ taken as 9.22 eV,[18] are listed in Table I. The ionization efficiency

Table III. Thermochemical Evaluation of the Gaseous Equilibrium Reaction PtY = Pt + Y

temp, K	$I_{Pt^+(195)}$, A	$I_{Y^+(89)}$, A	$I_{PtY^+(284)}$, A	ln K_p	$-\Delta[(G_T° - H_0°)/T]$, J mol^{-1} K^{-1}	$\Delta H_0°$, kJ mol^{-1}
2259	1.47×10^{-11}	7.05×10^{-12}	6.50×10^{-14}	−11.36	112.89	468.4
2264	2.15×10^{-11}	2.70×10^{-12}	4.50×10^{-14}	−11.57	112.89	473.4
2355	1.18×10^{-10}	8.10×10^{-12}	2.15×10^{-13}	−10.29	112.67	466.9
2364	1.45×10^{-10}	4.95×10^{-12}	1.70×10^{-13}	−10.34	112.64	469.5
2395	2.15×10^{-10}	6.15×10^{-12}	2.50×10^{-13}	−10.10	112.51	470.6
2395	2.20×10^{-10}	6.15×10^{-12}	2.15×10^{-13}	−9.93	112.51	467.2
2385	1.92×10^{-10}	6.45×10^{-12}	2.00×10^{-13}	−9.95	112.56	465.7
2378	1.89×10^{-10}	5.20×10^{-12}	2.10×10^{-13}	−10.23	112.58	470.0
2416	2.65×10^{-10}	7.50×10^{-12}	2.50×10^{-13}	−9.68	112.43	466.2
2456	3.67×10^{-10}	1.18×10^{-11}	3.80×10^{-13}	−9.30	112.26	465.7
2507	5.25×10^{-10}	2.50×10^{-11}	5.40×10^{-13}	−8.53	112.10	458.9
2499	5.22×10^{-10}	2.05×10^{-11}	5.40×10^{-13}	−8.77	112.12	461.8
2506	6.30×10^{-10}	2.70×10^{-11}	7.50×10^{-13}	−8.60	112.10	460.1
2514	6.90×10^{-10}	3.60×10^{-11}	9.00×10^{-13}	−8.40	112.08	457.4
2584	9.00×10^{-10}	4.15×10^{-11}	9.15×10^{-13}	−7.98	112.04	461.0
2684	1.20×10^{-09}	4.10×10^{-11}	7.20×10^{-13}	−7.43	112.54	467.8
2682	8.55×10^{-10}	1.32×10^{-10}	1.32×10^{-12}	−7.20	112.52	462.5
2704	8.40×10^{-10}	4.10×10^{-10}	4.25×10^{-12}	−7.25	112.74	467.9
2707	8.85×10^{-10}	8.00×10^{-10}	6.85×10^{-12}	−7.01	112.78	463.0
2736	6.90×10^{-10}	1.18×10^{-09}	7.65×10^{-12}	−6.96	113.16	468.0
						av 465.6 ± 4.1
						second law 475.1 ± 13.0

Table IV. Summary of Third-Law Evaluation of the Gaseous Equilibrium Reaction Pt_2 = 2Pt

temp, K	$I_{Pt^+(195)}$, A	$I_{Pt_2^+(390)}$, A	ln K_p	$-\Delta[(G_T° - H_0°)/T]$, J mol^{-1} K^{-1}	$\Delta H_0°$, kJ mol^{-1}
2456	4.20×10^{-10}	1.50×10^{-14}	−1.095	133.77	350.9
2507	5.25×10^{-10}	2.25×10^{-14}	−1.034	133.99	357.5
2585	7.80×10^{-10}	3.50×10^{-14}	−0.653	134.27	361.1
2684	1.80×10^{-9}	5.50×10^{-14}	0.605	134.57	347.7
2704	9.00×10^{-10}	1.95×10^{-14}	0.263	134.63	358.1
2707	8.85×10^{-10}	1.50×10^{-14}	0.493	134.64	353.4
					av 354.8 ± 4.6
					second law 357.9 ± 59.0

Table V. Summary of Third-Law Evaluations of the Gaseous Equilibrium Reaction PtY + Pt = Pt_2 + Y

temp, K	$I_{PtY^+(284)}$, A	$I_{Pt^+(195)}$, A	$I_{Pt_2^+(390)}$, A	$I_{Y^+(89)}$, A	ln K_p	$\Delta[(G_T° - H_0°)/T]$, J mol^{-1} K^{-1}	$\Delta H_0°$, kJ mol^{-1}
2456	3.80×10^{-13}	4.00×10^{-10}	1.50×10^{-14}	1.18×10^{-11}	−8.03	21.07	112.1
2507	5.40×10^{-13}	5.32×10^{-10}	2.25×10^{-14}	2.50×10^{-11}	−7.51	21.08	103.7
2585	9.15×10^{-13}	8.40×10^{-10}	3.50×10^{-14}	4.15×10^{-11}	−7.54	21.10	107.6
2684	7.20×10^{-13}	1.80×10^{-9}	5.50×10^{-14}	4.10×10^{-11}	−7.63	21.11	113.6
2704	4.25×10^{-12}	8.70×10^{-10}	1.95×10^{-14}	4.10×10^{-10}	−7.41	21.11	103.5
2707	6.85×10^{-12}	8.85×10^{-10}	1.50×10^{-14}	8.00×10^{-10}	−7.50	21.11	111.5
							av 109.7 ± 3.3
							second law 78.7 ± 40.6

curves for Pt_2^+ and PtY^+ showed no evidence of their fragmentation in the ion source. The experimental currents at the electron multiplier anode due to Pt^+ (*m/e* 195), Y^+ (*m/e* 89), PtY^+ (*m/e* 284), and Pt_2^+ (*m/e* 390) can be found listed as a function of temperature in Tables III–V.

Additional species observed were carbon molecules and platinum carbides. A typical set of relative ion currents is given in the sequence of measurements at 2704 K (*m/e* values in parenthesis) as follows: Pt (195) 1.03×10^{-9}; PtC_2 (219) 2.4×10^{-13}; PtC_3 (231) 1.6×10^{-13}; Pt_2 (390) 1.95×10^{-14} Pt (195) [9.00×10^{-10}] 8.85×10^{-10}; C^+ 1.95×10^{-10}; C_2^+ 1.12×10^{-10}; C_3^+ 1.95×10^{-9}; C_4^+ 6.15×10^{-12}; C_5^+ 6.15×10^{-12}; Y^+ 4.10×10^{-10}; PtY (289) 4.25×10^{-12}; Pt^+ (195) [8.40×10^{-10}] 8.20×10^{-10}; PtC^+ (207) 8.25×10^{-11}. The gaseous yttrium carbides species expected to be also present in the vapor[19] were not monitored in the present investigation. The results concerning the gaseous platinum carbides will be presented elsewhere,[20] together with those of the iridium carbides obtained in a different investigation. As can be seen from the above sequence of measured ion currents, the Pt^+ intensity decreased slightly during a set of measurements at the highest temperatures. The values for Pt (195) given in brackets next to the value for Pt_2^+ (390) and PtY^+ (284), respectively, have been interpolated to correspond to the instant of measurement of the respective molecular species (see also Tables III and IV). Likewise, an average Pt^+ (195) value has been used in the evaluation of reaction 3 to take this shift in Pt^+ intensity into account (see Table V). Other sets involving the Pt_2 molecule have been treated similarly. All the intensity data given in Tables III–V correspond to the sequence of measurements taken.

Several sets of Au^+ and Au_2^+ ion currents were measured in the 1489–1707 K temperature range for determining the instrument sensitivity through the gaseous equilibrium $Au_2(g) = 2Au(g)$.[21] With use of the literature data[22] for the enthalpy and the free-energy function change for this reaction, the pressure calibration constant, $k = P/I^+T$, for gold was determined as $k_{Au} = 4.12$ atm A^{-1} K^{-1}. The pressure constants for the other species were obtained from the relation $k_i = k_{Au}(\sigma_{Au}\gamma_{Au}E_i/\sigma_i\gamma_iE_{Au}n_i)$, where σ is the maximum ionization cross section, γ is the electron multiplier gain, E is the correction factor for converting the ion intensity measured at 19.3 eV to that corresponding to the maximum in the ionization efficiency curve, and n is the fractional isotopic abundance. The maximum ionization cross sections for Pt and Y were taken from Mann,[23] while those for Pt_2 and PtY were taken as 0.75 times the sum of the respective atomic cross sections.[24] The multiplier gains for Pt^+ and Y^+ were measured 6.39×10^4 and 9.70×10^4, respectively. For Pt_2^+ and PtY^+ it was assumed that $\gamma_{Pt_2} = \gamma_{Pt}$ and $\gamma_{PtY} = (\gamma_{Pt} + \gamma_Y)/2$. The correction factors E_i for all species were determined from their respective ionization efficiency curves. The experimental or estimated values of these parameters and the resulting pressure constants are listed in Table I.

Thermochemical Evaluation of Data

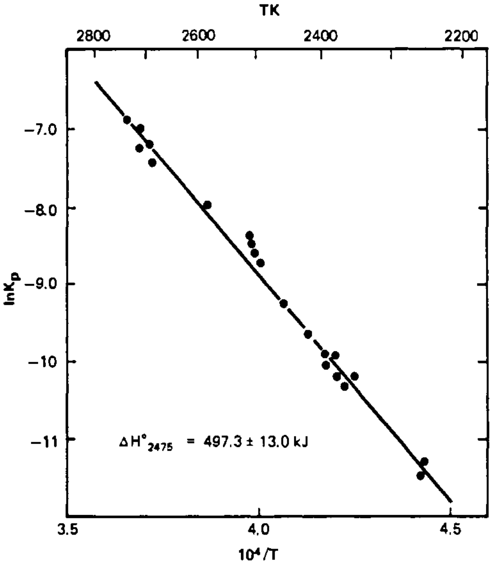

Figure 1. Second-law plot of the reaction $PtY(g) = Pt(g) + Y(g)$.

The experimental partial pressure data ($P_i = k_iI_i^+T$) were treated by the second- and third-law methods to derive the enthalpies of the gaseous equilibria (1)–(3) (see Figure 1).

$$PtY(g) = Pt(g) + Y(g) \tag{1}$$

$$Pt_2(g) = 2Pt(g) \tag{2}$$

$$PtY(g) + Pt(g) = Pt_2(g) + Y(g) \tag{3}$$

The necessary thermodynamic functions, $H_T° - H_0°$ and $(G_T° - H_0°)/T$, for Pt(g) and Y(g) were taken from the literature.[25] For $Pt_2(g)$ and PtY(g), these were calculated from estimated molecular parameters. The equilibrium bond lengths, r_e, were estimated on the basis of the spectroscopically determined bond length of the intermetallic molecule AuAl, $r_e = 2.338$ Å.[26] This observed bond length for AuAl is about 0.25 Å shorter than the sum of Pauling single-bond metallic radii[27] for Au and Al. Corresponding "bond shortenings" of 0.25 and 0.30 Å were estimated for $Pt_2(g)$ and PtY(g), respectively, by comparing the dissociation energy of AuAl(g), $D_0° = 332.2 \pm 6$ kJ mol^{-1},[28] with those expected for Pt_2 and PtY (370 and 450 kJ mol^{-1}, respectively) from preliminary evaluations of the present data. Thus the values $r_e(Pt-Pt) = 2.34$ Å and $r_e(Pt-Y) = 2.61$ Å were obtained. The vibrational frequencies, ω_e, were estimated from the Guggenheimer relation[29] for multiply bonded diatomic molecules (eq 4), where Z_1 and Z_2

$$\omega_e = 2976(Z_1Z_2)^{0.25}\mu^{-0.5}r_e^{-1.23} \quad (cm^{-1}) \tag{4}$$

are the number of outer electrons on each atom and μ is the reduced mass of the molecule in amu. With $Z_{Pt} = 6$ and $Z_Y = 3$ and the r_e values estimated above, the fundamental frequencies $\omega_e(Pt_2) = 259.4$ cm^{-1} and $\omega_e(PtY) = 241.0$ cm^{-1} were calculated. Electronic partition function for $Pt_2(g)$ was based on a $^1\Sigma$ ground state and a triplet excited stae lying 11 248.7 cm^{-1} above the ground state.[30] For PtY(g) the electronic contributions were based upon only a $^2\Sigma$ ground state neglecting any excited states. The calculated thermodynamic

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functions for the two molecules are listed in Table II.

The measured equilibrium constants and the derived enthalpy data for reactions 1–3 are given in Tables III–V. The uncertainties given for the third-law enthalpies and the second-law enthalpies are standard deviations. The probable error in the third-law values would be obtained by adding an uncertainty of 8 kJ mol^{-1}, corresponding to error estimates from all sources including free-energy functions, to the standard deviations shown.

In view of the large number of equilibrium measurements over an extensive temperature range (477 K) accomplished for reaction 1, the second-law $\Delta H_0°$ value must be considered very reliable. The good agreement between the second- and third-law values is taken as an indication of the validity of assumptions made in the estimation of the molecular parameters for the PtY molecule. By taking the mean of the two, we derive the selected values for the dissociation energy: $D_0°(\mathrm{PtY}) = 470 \pm 12$ kJ mol^{-1} or 112.4 ± 2.9 kcal mol^{-1}; $D_{298}°(\mathrm{PtY}) = 474 \pm 12$ kJ mol^{-1} or 113.2 ± 2.9 kcal mol^{-1}.

The excellent agreement between the second- and third-law enthalpies for reaction 2 is fortuitous as is evident from the very large standard deviation associated with the second-law value. The narrow temperature range and the small number of measurements on $Pt_2(g)$ do not allow a meaningful application of the second-law method to reactions 2 and 3. Combination of the third-law enthalpy of reaction 3, $\Delta H_0° = 109.7 \pm 7.3$ kJ mol^{-1}, with the dissociation energy of PtY(g) determined above leads to the dissociation energy of $Pt_2(g)$, $D_0° = 360.3 \pm 11.1$ kJ mol^{-1}. This value is in good agreement with the dissociation energy of 354.8 ± 8.6 kJ mol^{-1} yielded by the third-law evaluation of reaction 2. The mean of the two yields the selected values $D_0°(Pt_2) = 358 \pm 15$ kJmol^{-1} or 84.5 ± 3.6 kcal mol^{-1} and $D_{298}°(Pt_2) = 361 \pm 3.6$ kJ mol^{-1} or 86.3 ± 3.6 kcal mol^{-1}.

The dissociation energies of PtY and Pt_2 determined above, in combination with the heat of sublimation[25] of yttrium and platinum, lead to the following values for the standard heat of formation: $\Delta H_f°_{298}(\mathrm{PtY(g)}) = 516 \pm 12$ kJ mol^{-1} or 123.2 ± 2.9 kcal mol^{-1}; $\Delta H_f°_{298}(\mathrm{Pt_2(g)}) = 769 \pm 15$ kJ mol^{-1} or 183.7 ± 3.6 kcal mol^{-1}.

Discussion

$Pt_2(g)$. Gaseous Pt_2 has not been observed previously in mass spectrometry or optical spectroscopy experiments. Absorption spectra of matrix-isolated Pt_2 in the 8500–9000-Å region has been reported by Jansson and Scullman.[30] From the observed $A \leftarrow X$ absorption bands, they obtained a value of 216.6 cm^{-1} for the fundamental vibrational frequency of the A state of Pt_2 molecule. This would substantiate the value of $\omega_e = 259.4$ cm^{-1} estimated in the present work by the Guggenheimer relation[29] for Pt_2 in the ground state. It is seen from the ion intensities of Pt^+ and Pt_2^+ shown in Table IV, in conjunction with the respective pressure constants given in Table I, that the partial pressure of $Pt_2(g)$ is almost 5 orders of magnitude smaller than that of Pt(g) in the temperature range of 2456–2707 K. Thus in order to have a measurable concentration of $Pt_2(g)$ in the vapor above a platinum system, a combination of high temperatures and high platinum activity in the condensed system is necessary. In the previous mass spectrometric[31] and optical spectroscopic[32] investigations the failure to observe $Pt_2(g)$ is probably attributable to low activity of platinum because of its reaction with the container materials. A comparison of the partial pressures of Pt(g) measured in this work with the vapor pressure of pure platinum[25] indicates that the activity of platinum in our condensed system was relatively high, about 0.25 at 2507 K.

The dissociation energy of $Pt_2(g)$ determined in the present study is in accord with the overall trends found for the transition-metal dimers in that it is higher than the dissociation energy of Pd_2 ($D_0° = 104.6 \pm 20.9$ kJ mol^{-1}[28]), the second row congener of Pt_2, and than that of Au_2 ($D_0° = 221.3 \pm 2.1$ kJ mol^{-1}[22]) on the right side in the third row. In the valence-bond approach, the bonding in transition-metal dimers can be described as a multiple bond formed between two atoms in a d^ns state. Thus, in the Pt_2 molecule a double bond, a 6s–6s and a 5d–5d bond, is formed between two Pt atoms in the $5d^96s$ state. The unusually small dissociation energy of Pd_2 results due to the considerable amount (78.5 kJ mol^{-1}[18]) of energy needed to promote the Pd atom to a $4d^96s$ state, in addition to the lower bonding efficiency of 4d orbitals relative to that of 5d orbitals. On the other hand, in Au_2 only a 6s–6s bond is possible between Au atoms in the $5d^{10}6s$ state. The dimer dissociation energy would be expected to increase as one moves to the left of Pt in the third transition due to an increase in the number of unpaired d electrons becoming available for bonding. Krasnov[33] has correlated the known dissociation energies of transition-metal dimers through an empirical relation between the atomization energies and the valence-state promotion energies. The experimental value of the dissociation energy of Pt_2, $D_0° = 358 \pm 15$ kJ mol^{-1}, is within the range of 377–285 kJ mol^{-1} calculated for Pt_2 by Krasnov. The value yielded by the atomic cell model of Miedema and Gingerich[14] for the dissociation energy of Pt_2, 292 kJ mol^{-1}, is somewhat lower than the experimental one.

PtY(g). The dissociation energy of PtY, $D_0° = 470 \pm 8$ kJ mol^{-1}, may be compared with that of IrY,[34] $D_0° = 454 \pm 10$ kJ mol^{-1}, and that of LaPt,[35] $D_0° = 496 \pm 21$ kJ mol^{-1}. With assumption of the valence states of d^9s for Pt, d^8s for Ir, and d^2s for Y or La, the empirical valence-bond model of Gingerich[13] yields the dissociation energies of PtY, LaPt, and IrY as 316, 423, and 451 kJ mol^{-1}, respectively. While there is good agreement between the calculated and the experimental values for IrY, the experimental dissociation energies of PtY and LaPt are significantly higher than the calculated ones, as has been found in the case of the other intermetallic molecules of platinum.[13] The dissociation energies for PtY, LaPt, and IrY predicted by the atomic cell model for intermetallic diatomic molecules[15,36] are 470, 484, and 522 kJ mol^{-1}, respectively. In this case, the calculated and the experimental values are seen to be in excellent agreement for PtY and LaPt, but the calculated dissociation energy is somewhat higher than the experimental one for IrY.

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Registry No. Pt_2, 12596-95-1; PtY, 12038-34-5.

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