rate constant for self-exchange. The absence of a similar effect with the $IrCl_6^{2-/3-}$ couple is in line with the lower sensitivity of the self-exchange rate for this couple to the nature and concentration of cations present.[10] This difference presumably reflects the greater diameter and lower charges of the reactants involved in $IrCl_6^{2-/3-}$ self-exchange.

Conclusions

The relative ease and simplicity of the method described here for estimating self-exchange rates are among its most attractive features. In principle the method would seem to offer rather general applicability to multiply charged reactants. However, attempts to apply the method to cationic reactants by confining them in polyanionic coatings have thus far proved less successful because of difficulties in preparing sufficiently long-lived coatings with polyanionic polymers. In addition, the current-potential responses observed for several cationic reactants confined within polyanionic films were less well-behaved than those obtained with anionic reactants in polycationic films. Nevertheless, we expect the present obstacles to more general application of the procedure described to be surmounted as more experience and practice with techniques for preparing polyelectrolyte-coated electrodes are acquired.

Acknowledgment. This work was supported by the National Science Foundation and the U.S. Army Research Office.

Registry No. $IrCl_6^{2-}$, 16918-91-5; $Fe(CN)_6^{3-}$, 13408-62-3; $IrCl_6^{3-}$, 14648-50-1; $Fe(CN)_6^{4-}$, 13408-63-4; PVP, 100-43-6.

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Dissociation Energy and Standard Heat of Formation of Gaseous LaPt

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Received December 13, 1979

The molecule LaPt was observed in the gas phase above the system Pt-La-graphite, by using the Knudsen effusion mass spectrometric technique in the temperature range of 1959-2466 K. The enthalpy change of the reaction LaPt(g) = La(g) + Pt(g) (or dissociation energy of LaPt(g)) was determined as ΔH°_0 (or D°_0) = 496 ± 21 kJ mol^{-1} or 118.5 ± 5.0 kcal mol^{-1}. The corresponding standard heat of formation of LaPt(g) was obtained as $\Delta H_f{}^\circ{}_{298}$ = 497 ± 21 kJ mol^{-1} or 118.7 ± 5.0 kcal mol^{-1}. The dissociation energy of gaseous LaPt is discussed in terms of empirical models of bonding.

Introduction

The physical and chemical properties of small transition-metal clusters have been the object of experimental and theoretical investigations in recent years because such clusters appear to play an important role in certain catalytic processes.[1] The knowledge of the bonding energies of diatomic metal molecules is fundamental and provides an important step in bridging the properties when going from metal atoms to small clusters and alloys. We have been engaged in the study of the dissociation energies of strongly bonded intermetallic molecules and in the interpretation of the values obtained in terms of empirical models of bonding. Two such models have been successful. The first is a valence-bond approach for multiply bonded diatomic molecules[2] which has been found applicable to the diatomic platinum metal compounds with the d-electron deficient transition metals of groups 3-5, the lanthanides, or the actinide metals. This model utilizes the electron bonding energies determined by Brewer[3] for the corresponding bulk metals and suitable valence states for the atoms that permit the formation of double bonds, triple bonds, and, to a restricted extent, quadrupole bonds. The sum of the necessary valence-state promotion energies is subtracted from the sum of the electron bonding energies, yielding the calculated dissociation energy. The second model[4] is based on the atomic cell model developed by Miedema and associates for calculating enthalpies of formation of solid or liquid alloys.[5] Both models encounter difficulties when applied to platinum compounds of the more electropositive transition metals. For such molecules the valence-bond model tends to underestimate the dissociation energy,[6] while the atomic cell model tends to overestimate it.[4]

In the present investigation we have therefore determined the dissociation energy of gaseous LaPt by Knudsen effusion mass spectrometry in order to enlarge the experimental basis to understand the bond energies in platinum metal compounds with group 3 transition metals[7-10] and possibly refine the available empirical models of bonding. A previous estimate for the dissociation energy of LaPt by the valence-bond model yielded 423 kJ mol^{-1},[11] whereas the atomic cell model results in 573 kJ mol^{-1} when the parameters in ref 4 are used.

Experimental Section

The system Pt-La-graphite was studied by using a single-focusing 90° magnetic-sector mass spectrometer (Nuclide 12-90 HT) described previously.[12,13] The graphite-lined tantalum-carbide-coated tantalum Knudsen cell, with a 1.0-mm orifice diameter, was loaded with platinum wire (100 mg), lanthanum sheet (20 mg), graphite powder (50 mg), and, for the pressure calibration, 15 mg of gold.

The cell was heated by a tungsten coil formed from a rod with a diameter of 3.2 mm. The temperature was measured with a Leeds and Northrup optical pyrometer focused on a black-body hole in the bottom of the Kundsen cell. A calibration of the pyrometer was made in a previous run by measuring the vapor pressure of gold at its melting point. For this purpose a 3-g sample of gold (NBS standard for vapor pressure calibration) was placed in a graphite cell with thin walls (ca. 0.5 mm) in order to permit the observation of the temperature plateau during melting and freezing of the gold. The molecular beam was

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Table I. Measured and Estimated Parameters for Relevant Species over the Pt–La–Au–C System

ion	appearance potential, eV	ionization cross section σ_i, Å	multiplier gain γ_i		intens correction factor E_i	pressure const k_i	
			run I	run II		run I	run II
Au^+	9.22	5.85	6.4×10^4	1.14×10^5	1.05	2.48	1.60
Pt^+	8.9 ± 0.5	6.60	7.01×10^4 [b]	1.25×10^5 [b]	1.19	6.73	4.34
La^+	5.9 ± 0.7	16.07	9.22×10^4	1.64×10^5	1.00	0.60	0.38
$LaPt^+$	5.4 ± 0.8	17.00	8.11×10^4 [a]	1.45×10^5 [a]	1.01	1.92	1.24

[a] Estimated parameters. [b] Value taken in a previous run.[8]

Table II. Ion Intensities (in A) and Third Law Evaluation of the Gas-Phase Equilibrium LaPt = La + Pt (Run I)[a]

temp, K	$I^+_{LaPt(334)}$	$I^+_{Pt(195)}$	$I^+_{La(139)}$	$-\log K_p$	$-\Delta[(G^\circ_T - H^\circ_0/T)]$, J mol⁻¹ K⁻¹	ΔH°_0,[b] kJ mol⁻¹
2225	1.75×10^{-13}	9.60×10^{-13}	5.95×10^{-11}	5.82	109.96	492.51
2256	5.55×10^{-13}	2.75×10^{-12}	8.73×10^{-11}	5.69	110.26	494.51
2268	8.55×10^{-13}	3.75×10^{-12}	1.14×10^{-10}	5.63	110.37	494.58
2316	1.56×10^{-12}	6.95×10^{-12}	1.90×10^{-10}	5.39	110.85	495.61
2276	5.85×10^{-12}	3.45×10^{-12}	9.60×10^{-11}	5.57	110.45	494.08
2296	7.35×10^{-13}	4.70×10^{-12}	1.30×10^{-10}	5.40	110.65	491.31
2354	1.75×10^{-12}	9.75×10^{-12}	2.30×10^{-10}	5.20	111.22	496.18
2428	4.01×10^{-12}	2.65×10^{-11}	4.22×10^{-10}	4.85	111.87	497.02
2466	6.15×10^{-12}	4.70×10^{-11}	5.95×10^{-10}	4.63	112.14	495.13
						av 494.5 ± 1.6

[a] $P_i = k_i I^+ T$ (in atm, see Table I for k_i values). [b] Second law $\Delta H^\circ_0 = 477.6 \pm 15.4$ kJ mol⁻¹.

Table III. Ion Intensities (in A) and Third Law Evaluation of the Gas-Phase Equilibrium LaPt = La + Pt (Run II)[a]

temp, K	$I^+_{PtLa(334)}$	$I^+_{Pt(195)}$	$I^+_{La(139)}$	$-\log K_p$	$-\Delta[(G^\circ_T - H^\circ_0)/T]$, J mol⁻¹ K⁻¹	ΔH°_0,[b] kJ mol⁻¹
2242	2.05×10^{-12}	7.80×10^{-12}	1.15×10^{-10}	5.88	110.12	499.21
2106	6.60×10^{-13}	1.40×10^{-12}	3.30×10^{-11}	6.70	109.00	499.75
2096	6.30×10^{-13}	1.15×10^{-12}	2.68×10^{-11}	6.86	108.94	503.58
1959	2.70×10^{-13}	1.50×10^{-13}	1.07×10^{-11}	7.81	108.68	505.67
1991	3.90×10^{-13}	4.35×10^{-13}	1.30×10^{-11}	7.41	108.63	498.73
2064	5.04×10^{-13}	7.74×10^{-13}	1.65×10^{-11}	7.15	108.78	507.12
2101	5.34×10^{-13}	1.68×10^{-12}	2.28×10^{-11}	6.70	108.97	498.12
2201	1.70×10^{-12}	5.25×10^{-12}	7.56×10^{-11}	6.16	109.73	501.06
2271	2.81×10^{-12}	1.00×10^{-11}	1.54×10^{-10}	5.77	110.40	501.76
2333	6.15×10^{-12}	2.18×10^{-11}	3.05×10^{-10}	5.48	111.02	503.25
2141	1.35×10^{-12}	4.00×10^{-12}	4.65×10^{-11}	6.40	109.23	496.22
2211	2.58×10^{-12}	8.70×10^{-12}	8.40×10^{-11}	6.07	109.82	499.91
2283	5.10×10^{-12}	1.35×10^{-11}	1.85×10^{-10}	5.82	110.52	506.78
						av 501.6 ± 3.3

[a] $P_i = k_i I^+ T$ (in atm, see Table I for k_i values). [b] Second law $\Delta H^\circ_0 = 500.9 \pm 18.5$ kJ mol⁻¹.

ionized by 19-V electrons at an electron emission current of 0.3 mA. The ions, accelerated by a 4.5 kV potential, were detected by a 20-stage Be–Cu dynode electron multiplier, whose entrance shield was maintained at about 2.5 kV. The species studied were identified by their shutter profile, appearance potential, mass to charge ratio, and isotopic abundance. The intensities of Au_2^+ and Au^+ were measured in the range 1809–2225 and 1601–1926 K during the first and second run, respectively, for the purpose of determining the instrument sensitivity by utilizing the dissociation equilibrium $Au_2(g) = 2Au(g)$,[14] by using the literature data for the dissociation energy $D^\circ_{298}[Au_2(g)] = 53.46 \pm 0.25$ kcal mol⁻¹,[15] and for the free energy functions of $Au_2(g)$[15] and Au(g).[16] The calculated pressure constants ($k = P/I^+T$) in atm A⁻¹ K⁻¹ were $k_{Au}(I) = 2.048 \pm 0.38$ and $k_{Au}(II) = 1.60 \pm 0.29$. For the other species the pressure constants were determined by the relation

$$k = k_{Au} \frac{\sigma_{Au} \gamma_{Au} E_i}{n_i \sigma_i \gamma_i E_{Au}}$$

where σ is the maximum ionization cross section, γ is the multiplier gain, n is the isotopic abundance, and E is an intensity correction factor obtained as the ratio between the intensity at the maximum ionization potential and the measured one. For Pt and La, Mann's[17] atomic cross sections were used, while for LaPt, σ was calculated by multiplying the sum of the atomic cross sections by 0.75.[18] The multiplier gains for the atoms were measured, and for LaPt it was taken as the average of those of Pt and La. All these values are shown in Table I.

Results

The molecule LaPt was first detected at 2225 K and identified by the isotopic distribution and the appearance potential determined from the ionization efficiency curve by the linear extrapolation method relative to that of Au taken as 9.22 eV.[3] For evaluation of the dissociation energy of LaPt, the intensities of the ions $LaPt^+$, Pt^+, and La^+ at mass to charge ratios 334, 195, and 139, respectively, were measured as a function of temperature. In Table II and III these are listed for the two runs, together with the derived reaction enthalpies. For Pt(g) and La(g) the free energy functions used in the third law evaluation were taken from Hultgen et al.[16] while those for LaPt were calculated by standard statistical thermodynamic equations with use of estimated molecular parameters. The LaPt bond distance was estimated equal to 2.62 Å from the Pauling radii[19] by utilizing a bond shortening correction

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

temp, K	$-(G°_T - H°_0)/T$	$H°_T - H°_0$
298.15	247.87	9.845
2000	314.91	73.207
2100	316.69	76.946
2200	318.39	80.685
2300	320.02	84.424
2400	321.59	88.164
2500	323.09	91.903
2600	324.53	95.643

of 0.36 as for LaIr.[7] The vibrational frequency was calculated according to the Guggenheimer relation[20] for diatomic molecules with a multiple bond and resulted in ω_e = 280.6 cm^{-1}. The *z* values used were 6 for Pt and 3 for La. According to the Wigner and Witmer procedure, as described by Herzberg,[21] for the determination of the multiplicity of atoms, the possible states for LaPt are $^2\Sigma$ and $^4\Sigma$.

Here the calculation for the electronic partition function has been based on a $^4\Sigma$ ground state because of the possible contribution from low-lying excited states. The free-energy functions and heat contents for LaPt(g) are shown in Table IV.

The dissociation equilibrium LaPt(g) = La(g) + Pt(g) was treated by the third law method, according to the equation $\Delta H°_0 = -RT \ln K_p - T\Delta[(G°_T - H°_0)/T]$, which yielded the values $\Delta H°_0$ = 494.5 ± 1.6 kJ mol^{-1} or 118.2 ± 0.4 kcal mol^{-1} and 501.6 ± 3.3 kJ mol^{-1} or 119.9 ± 0.8 kcal mol^{-1} for run I and run II, respectively, where the error terms correspond to the standard deviations.

From the second law treatment according to the relation $d \ln K_p/d(1/T) = -\Delta H°_T/R$, $\Delta H°_0$ = 477.6 ± 15.4 kJ mol^{-1} or 114.1 ± 3.7 kcal mol^{-1} was obtained for the first run while for the second run the enthalpy change was $\Delta H°_0$ = 500.9 ± 18.5 kJ mol^{-1} or 119.7 ± 4.4 kcal mol^{-1}, where the errors are the standard deviations from the least-squares analysis.

The selected value for the dissociation energy was taken as the weighted mean of the second and third law data of both runs $\Delta H°_0$ = 496 ± 21 kJ mol^{-1} or 118.5 ± 5.0 kcal mol^{-1}. The associated error is obtained adding an uncertainty of 12 kJ mol^{-1} to the weighted error, taking into account all the probable errors including those in the temperature and in the free energy functions. The weight given the second law value of the first run was taken as 0.5 in the weighted mean because of the shorter temperature range and fewer points in the second law plot. Considering the $D°_{298}$ = 499 ± 21 kJ mol^{-1} or 119.3 ± 5.0 kcal mol^{-1} and with the platinum and lanthanum sublimation enthalpies from Hultgren[16] the standard enthalpy of formation of gaseous LaPt was derived as $\Delta H_f°_{298}$ = 497 ± 21 kJ mol^{-1} or 118.7 ± 5.0 kcal mol^{-1}. In Table V the second and third law enthalpy and entropy data have been summarized.

Discussion

Of the two runs the second law result of run II is considered the more reliable one because of the larger number of data sets and temperature range, respectively, as compared with run I. In run II this is borne out by the good agreement between the ΔH values derived from the second and third law evaluations. The average enthalpy change of the LaPt dissocation reaction, obtained in the second run agrees also with the third law value of the first run.

Table V. Summary for the Second and Third Law Evaluations of the Gas-Phase Reaction LaPt = La + Pt[a]

	run I	run II
temp range, K	2225–2466	1959–2333
av temp, K	2339	2130
$\Delta H°_T$, kJ mol^{-1}	514.4 ± 15.4	533.9 ± 18.5
$\Delta S°_T$, J mol^{-1} K^{-1}	119.4 ± 6.6	124.6 ± 8.6
$\Delta S°_{298}$, J mol^{-1} K^{-1} (2nd law)	86.3 ± 6.6	93.6 ± 8.6
$\Delta S°_{298}$, J mol^{-1} K^{-1} (3rd law)	93.7	93.7
$\Delta H°_{298}$, kJ mol^{-1} (2nd law)	480.7 ± 15.4	503.9 ± 18.5
$\Delta H°_{298}$, kJ mol^{-1} (3rd law)	497.6 ± 1.6	504.6 ± 3.3
$\Delta H°_0$, kJ mol^{-1} (2nd law)	477.6 ± 15.4	500.9 ± 18.5
$\Delta H°_0$, kJ mol^{-1} (3rd law)	494.5 ± 1.6	501.6 ± 3.3

[a] Selected value $\Delta H°_0$ = 496 ± 21 kJ mol^{-1} or 118.5 ± 5.0 kcal mol^{-1}.

The agreement between the second and third law together with the fact that there is no noticeable temperature trend in the third law reaction enthalpies may be taken as a confirmation of the choice of the molecular parameters used for the calculations of the free energy functions. Here the LaPt multiple bond has been assumed to be partially ionic with Pt in the state 5d^{10}6s and La in the state 5d6s.

The experimental value for $D°_0$(LaPt) of 496 ± 21 kJ mol^{-1} is between the respective values of 423 and 573 kJ mol^{-1} estimated by the valence-bond model and by the atomic cell model. The value estimated by the valence-bond model has been based on an assumed double bond for LaPt,[11] for lack of a suitable valence state of Pt for triple-bond formation. It has been pointed out elsewhere,[6] with use of the pair CeIr(g) and CePt(g) for illustration, that a better agreement with the experimental result is obtained when the calculated bond energy of the platinum intermetallic group 3 molecule is based on the corresponding iridium compound instead of the platinum compound, since iridium has a suitable valence state for triple-bond formation. The value for the corresponding LaIr molecule ($D°_0$ = 574 ± 12 (exptl)[7] or 565 kJ mol^{-1} (calcd)[11] is then qualitatively corrected downward for the presence of an additional antibonding electron. Here a formal bond order of 6 is assumed for LaIr with use of the molecular orbital approach and consequently a bond order of 5$^1/_2$ for LaPt. The lower value of $D°_0$(LaPt) as compared to LaIr (about 80 kJ mol^{-1}) appears to correspond to somewhat more than half a bond but is not unreasonable.

The value calculated for LaPt with use of the atomic cell model is too high, as may be expected for molecules of electropositive transition metals such as La, with very electronegative metals such as Pt and Au, at the end of a transition element series. In LaPt, platinum may be thought to transform from a high-valence transition metal to a low-valence transition metal with a completed d-shell upon accepting charge from lanthanum.[4] This effect is not expected to be operative in the molecules TaOs or WRe which are isoelectronic with LaPt but for which the electronegativity difference of the component atoms is small. The respective dissociation energies calculated by the atomic cell model for TaOs and WRe are 513 and 436 kJ mol^{-1},[4] in fair agreement with the experimental value for LaPt. Since the completion of this work, Miedema[22] has independently considered this effect and presented a revised calculated dissociation energy for LaPt of 484 kJ mol^{-1}, in good agreement with the experimental value.

Acknowledgment. We thank D. Satish K. Gupta for valuable discussions and the National Science Foundation for the support of this work under Grant CHE 78-08711. B.M.N. also thanks the CIES for a Fulbright grant.

Registry No. LaPt, 12142-67-5.

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