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MASS SPECTROMETRIC EVIDENCE FOR THE VERY HIGH STABILITY OF GASEOUS ThIr AND ThPt AND METHOD OF CALCULATING DISSOCIATION ENERGIES OF DIATOMIC INTERMETALLIC COMPOUNDS WITH MULTIPLE BONDS

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Mass Spectrometric Evidence for the Very High Stability of Gaseous ThIr and ThPt and Method of Calculating Dissociation Energies of Diatomic Intermetallic Compounds with Multiple Bonds

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The dissociation energies, D_0°, of the molecules ThIr and ThPt have been measured by high temperature Knudsen cell mass spectrometry as 138.4 ± 10 and 132.8 ± 8 kcal mol^{-1} or 579.1 ± 41.8 and 555.6 ± 33.5 kJ mol^{-1}, respectively.

A method is proposed for the calculation of dissociation energies of gaseous intermetallic compounds with multiple bonds.

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INTRODUCTION

The present investigation had its objective to identify molecules between atoms of metallic elements with exceptionally high bond energies under equilibrium conditions and to determine their bond dissociation energies.

In recent years there has been considerable interest in strong metal-metal bonds between pairs of metal atoms in complex compounds(1) as well as between ligand free metal atoms(2). For the strongest bonds between pairs of like metal atoms in complex compounds, e.g. molybdenum or rhenium, convincing evidence has been presented for the presence of quadruple bonds on the basis of the distance between the atoms, molecular geometry and considerations of molecular orbital theory. No bond energies have, however, yet been measured for such compounds and Cotton(1) has suggested that the bond energy holding the pair of metal atoms together may be as high as 400 kcal mol^{-1}. An attempt to estimate values for bond energies of these reported metal-metal quadruple bonds has been made on the basis of an assumed analogy between internuclear distance and corresponding bond energy in ligand free diatomic molecules and a pair of metal atoms in complex compounds, resulting in values of the order of 100 to 200 kcal mol^{-1}.(3)

The search of ligand free molecules with multiple metal-metal bonds has recently been stimulated by the predictions of the Brewer-Engel metallic theory of particularly strong bonding in alloy systems between metals at the beginning of a transition series, lanthanides or actinides with platinum group metals.(4,5) Its suggested extension(6) to gaseous intermetallic compounds has been confirmed for the molcules LuPt(7), CePd(8), and TiRh(9).

EXPERIMENTAL

In view of the established or predicted high stability of zirconium and thorium compounds with platinum, rhodium, or iridium,(5,10) an alloy with the approximate composition $(Zr,Th)(Pt,Ir,Rh)_2$ was chosen in this investigation as a source of very stable intermetallic molecules and was evaporated from a graphite Knudsen cell that was inserted in a tantalum cell(11). The instrument, the experimental procedure and the treatment of data used have been described elsewhere.(8,12) The electron energy used was 20 ev.

Thorium containing intermetallic compounds were observed at 2770K and the relative intensities together with those of other pertinent species were measured as follows, giving for the thorium containing intermetallic compounds also the measured isotopic distribution: C^+, 56,900; Rh^+, 18,300; $^{194}Pt^+$, 4,800; RhC^+, 1,000; $^{194}PtC^+$, 450; Th^+, 400; $^{193}Ir^+$, 250; $^{193}IrC^+$, 140; $^{195}PtTh^+$, 4.5; $^{194}PtTh^+$, 4.6; $^{196}PtTh^+$, 3.3; $ThRh_2^+$ (tentative), 1.9; $^{198}PtTh^+$, 1.1; $^{193}IrTh^+$, 0.8, and $^{193}IrTh^+$, 0.5. The appearance potential of ThPt was measured as 8±2 e.v. The intensity of $ThIr^+$ was too small for an appearance potential measurement.

The ions $ThRh^+$, $ZrRh^+$, $ZrIr^+$ and $ZrPt^+$ could not be detected using a sensitivity corresponding to a relative ion current of about 30. The ion current of $^{90}Zr^+$ measured at a lower temperature was found to be between 10 and 100 times less than that of Th^+.

RESULTS

These ion currents, which correspond to maximum ionization were used to calculate the third law enthalphies for the reactions involving ThPt and ThIr as reactants shown in Table I. Preliminary measurements at lower temperatures had also indicated that the difference in the dissociation energies of IrC and PtC was measurably larger than that calculated from the results by Drowart and collaborators.(13,14) Therefore several sets were measured for the exchange reactions between these molecules and RhC shown in Table II, in order to redetermine their dissociation energy,using the well established one for RhC(13,15) as a standard. These redetermined values for PtC and IrC were then combined with the respective reaction enthaphies in Table I to obtain the dissociation energies for ThPt and ThIr,respectively.

In the calculation of equilibrium constants for the reactions shown in Tables I and II, it was assumed that the effects of ionization cross sections and multiplier gains cancel. The free energy functions were taken from literature for the atoms(16,17) and the MC molecules.(13-15) Those for ThPt, ThIr and ThRh were calculated from estimated molecular parameters by means of standard statistical thermodynamic relations. On the basis of the estimated molecular parameters (r_e, 2.54, 2.51 and 2.51 Å; ω_e, 221, 215, and 252 cm^{-1}, respectively), and an assumed electronic contribution of 3 e.u., the following $-(G^\circ_T-H^\circ_0)/T$ values, in e.u, were obtained for 2600K and 2800K, respectively: ThPt, 79.48 and 80.13; ThIr, 79.36 and 80.01; and ThRh, 77.59 and 78.25.

Combining the resulting reaction enthalpies in Table I with the appropriate dissociation energies of PtC and IrC of Table II, the dissociation energies, D°_0, for ThPt and ThIr are obtained as 132.8±8 and 138.4±10 kcal mol^{-1} or 555.6±33.5 and 579.1±41.8 kJ mol^{-1}. Basing the dissociation energies of ThPt and ThIr on the literature values: $D^\circ_0(PtC)=145.3\pm1.5$ kcal mol^{-1}(13) and $D^\circ_0(IrC)=148.4\pm3.0$ kcal mol^{-1}(14) would yield 133.5 and 137.4 kcal mol^{-1}, respectively.

The results obtained here for $D^\circ_0(PtC)$ and $D^\circ_0(IrC)$ agree individually with the literature values within the limits of stated error. But the differences in the two dissociation energies derived here is larger (4.7±0.4 kcal) than the corresponding difference of 3.1 kcal between the literature values. The overall error in this difference is judged to be less than twice the standard deviation, that is less than ±0.8 kcal. In further support for the preference for the $D^\circ_0(PtC)$ and $D^\circ_0(IrC)$ values obtained in this investigation it is noted that due t the high symmetry of the pressure independent reactions in Table II possible systematic errors are very small, and that there is no danger of deviations of the activity of carbon from unity. Further support for this conclusion comes from the reaction enthalpies shown in Table I, by noting that the directly determined difference in the dissociation energies of ThPt and ThIr is not consistent with the difference calculated when basing these dissociation energies on the literature values for $D_0^\circ(PtC)$ and $D_0^\circ(IrC)$.

The comparatively large error terms chosen for $D_0^\circ(ThPt)$ and $D_0^\circ(ThIr)$ reflect mainly the uncertainty coming from the unknown electronic contribution to the free energy functions of these molecules and the limited amount of data that was possible to be obtained under the extreme experimental conditions used. Again, it is noted that the accuracy of difference in the dissociation energies of these two molecules is much better, provided there is no large difference in the electronic contribution to the free energy functions of these two molecules. Assuming no electronic contributions, the dissociation energies of ThPt and ThIr would become 138.8 and 146.4 kcal mol^{-1}, respectively.

For the molecule ThRh an upper value for the dissociation energy has been calculated as < 130 kcal mol^{-1} assuming no electronic contribution to the free energy function. Approximate upper values for the not observed molecules ZrRh, ZrPt and ZrIr are 145, 150 and 155 kcal mol^{-1}, respectively. The dissociation energies reported here for ThPt and ThIr represent the largest measured so far for a metal to metal bond. They suggest a double or triple bond for ThPt and a triple bond for ThIr (See below).

METHOD OF CALCULATING DISSOCIATION ENERGIES OF DIATOMIC INTERMETALLIC COMPOUNDS WITH MULTIPLE BONDS

To account for the measured bond dissociation energies in the diatomic intermetallic compounds with multiple bonds a method is proposed that is analogous to the one used by Brewer for the calculation of the bonding energies of condensed metals.(4,18,19) The method is based on the valence bond theory. Each of the two atoms forming the molecule is promoted to a valence state with two to four unpaired electrons that is suitable for multiple bond formation. These electrons are then allowed to form electron pair bonds with the unpaired electrons of the valence state of the second atom. The resulting bond energy per electron pair per mole is then taken the same as the determined valence state bonding enthalpy in kcal per mole per electron for the corresponding type of electrons in the respective condensed metal.(19) The individual values for the latter are taken from the Brewer curves which show the variation of s or p and d valence state bonding enthalpies per mole of electrons with atomic number and with principle quantum number, and in case of the d-electrons, also with the number of d-electrons participating in the bonding. Wengert has conveniently tabulated most of these values.(20) Since the atoms forming the diatomic molecules belong to different elements, the additional assumption is made in the present method that for each bond the average is taken of the individual valence state bonding enthalpies for the two electrons from the two different atoms that form the electron pair bond. The bonding energies of all bonds formed are then added. From this sum, the sum of the valence state promotion energies is subtracted. The resulting value represents the calculated dissociation energy. The necessary valence state promotion energies are taken from literature.(21,22) They are evaluated in an analogeous manner as shown by Brewer.(18,19)

The method has been applied to the diatomic intermetallic compounds determined or searched for in the present investigation and to the other intermetallic compounds for which measurements of the dissociation energy have indicated the presence of a bond order larger than one.(7-9,23) The calculated values are given in Table III and compared with the experimental values where available. For the thorium compounds it was assumed that the 6d-electrons form stronger bonds as 5d-electrons in analogy to the trend observed when going from 3d to 5d electrons.(4,5,10,18,19)

The agreement between calculated and experimental values is quite good except that the experimental dissociation energies for the platinum containing molecules are somewhat larger as the calculated ones. For ThRh the calculated value appears to be somewhat too high; it indicates that under the conditions used the ion intensity of the molecule $ThRh^+$ must have been near the detection limit whereas that for the zirconium containing platinum metal compounds was probably considerably below it. High bond energies are also expected for lanthanum and cerium compounds with most platinum metals since both, lanthanum and cerium require only a small promotion energy to a valence state that is suitable for formation of a triple bond (and for cerium in case of f-electron involvement possibly also for a quadruple bond with ruthenium or osmium).

It is revealing to speculate which will be the diatomic intermetallic compounds with the largest dissociation energies. From the evidence presented for certain pairs of atoms in complex compounds(1) it is reasonable to assume that the formation of four bonds represents the maximum possible bond order between two metal atoms. Suitable valence states permitting formation of four bonds and that require no or small promotion energies are for example available for Ru and Os on one hand and Th and Nb on the other hand. Some calculated dissociation energies for molecules with assumed quadruple bonds have been included in Table III.

The procedure outlined here for calculating dissociation energies of certain diatomic intermetallic compounds has not taken into account the possibility of forming bonds in which non bonding electrons on the platinum group metal are utilized by vacant d orbitals on the left side transition metal, lanthanide or actinide metal. Such an effect is difficult to estimate quantitatively. It might be considered implicit in the procedure outlined here by limiting it to molecules between metals with vacant d-orbitals and those containing paired d-electrons.

The experimental values for LuPt and ThPt suggest, that strengthening of bonding by such a "Lewis acid-base" effect(10) may occur explicitly in case of platinum where the promotion energy to a valence state suitable for triple or quadruple bond formation is too large to be offset by the formation of the additional bonds. The experimental observation appears to indicate that interaction of a non-bonding electron pair from Pt with a vacant d-orbital on Lu or Th to form a dative bond leads to a net gain in bonding energy over that calculated for a double bond. In view of the established increase of d-electron bonding energies with principle quantum number such additional bond formation may be expected especially for molecules utilizing 5d and 6d electrons in bonding.

The principle value of the procedure used appears to be toofold:(a) It indicates important connections in the nature of bonding in condensed metals and in isolated pairs of metals, and (b) it can be used to predict actual bond energies of diatomic intermetallic molecules with multiple bonds. Theoretical and spectroscopic investigations will be necessary in order to obtain a deeper and more detailed understanding of the nature bonding in such molecules.

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Table I

Third law enthalpies of reactions involving ThPt and ThIr at 2770 K.

Reaction	log K_p	$-\Delta[(G^\circ_{2770}-H^\circ_0)/T]$ cal K^{-1}	ΔH kcal
$ThPt(g) + C(g) = PtC(g) + Th(g)$	0.047	-5.01	-11.8
$ThIr(g) + C(g) = IrC(g) + Th(g)$	0.332	-3.56	-11.0
$ThPt(g) + Ir(g) = ThIr(g) + Pt(g)$	0.476	+0.29	- 5.8

Table II

Third law enthalpies of reactions between platinum metal monocarbides.

Reaction	Temperature range (°K)	No. of data sets	ΔH_0° kcal	$D_0^\circ(M)$ kcal/mol	M
$RhC(g) + Pt(g) = PtC(g) + Rh(g)$	2631-2775	5	-6.1±0.4	144.6±2.5[a)]	PtC
$RhC(g) + Ir(g) = IrC(g) + Rh(g)$	2631-2775	5	-10.7±0.3	149.2±2.5[a)]	IrC
$PtC(g) + Ir(g) = IrC(g) + Pt(g)$	2631-2775	5	-4.7±0.4	149.3±2.5[b)]	IrC

a) using $D_0^\circ(RhC) = 138.5 \pm 2$ kcal mol^{-1}, References 13 and 15.

b) using $D_0^\circ(PtC) = 144.6 \pm 2.5$ kcal mol^{-1}, this investigation

Table III

Comparison of experimental and calculated dissociation energies of selected intermetallic compounds with multiple bonds.

Molecule	Assumed Bond Order	D_0°(calc.) kcal mol^{-1}	D_0°(exp.) kcal mol^{-1}
LuPt	2	85	95 ±8[a)]
CePd	2	78	76.1±4[b)]
TiRh	3	92	92.5±3.5[c)]
LaRh	3	129	125.4±4[d)]
ThRh	3	131	< 130 ± 10[e)]
ThPt	2	117	133.5±8[e)]
ThIr	3	137	138.4±10[e)]
ZrRh	3	117	< 145 ± 10[e)]
ZrPt	2	97	< 150 ± 10[e)]
ZrRu	4	141	
ThRu	4	161	
ThOs	4	157	
NbRu	4	155	
NbOs	4	153	

a) Refernece 7

b) Reference 8

c) Reference 9

d) Reference 23

e) This investigation