Mass Spectrometric Determination of Bond Energies of High-Temperature Molecules*

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Abstract

The application of the KNUDSEN cell mass spectrometric method for measuring bond energies of high-temperature molecules is described. Selected recent results are presented and discussed in terms of empirical models of bonding.

Introduction

The present paper describes the application of the KNUDSEN cell method combined with mass spectrometric analysis of effusing vapors for the determination of bond energies of high-temperature molecules. The work reported concerns investigations in which the author has been active during the last few years. Thus it is not intended to be a review of the subject. There are of course other important methods for determining bond energies of high temperature molecules which utilize mass spectrometric analysis. Of these, two are mentioned: investigation of the energetics of electron impact processes and photoionization mass spectrometry. The former can be widely used for quite complex molecules that are not necessarily stable at high temperatures but great care must be taken a) in the interpretation of the fragmentation process that leads to the ions measured by mass spectrometry and b) in the interpretation and precise measurement of appearance potentials. In experiments where electron impact and KNUDSEN cell methods were both applied to the mass spectrometric determination of the bond energies of given molecules, the electron impact method has tended to give less reliable results.

Photoionization mass spectrometry, when applied to the measurement of bond energies of high temperature molecules requires these to be present in comparatively large concentrations. In addition, some knowledge concerning the electronic and molecular parameters of the products is necessary. The resulting bond energies of the molecules measured may be considerably more accurate than those obtained by KNUDSEN cell mass spectrometry, although comparatively large discrepancies have occasionally been reported for the same molecule by different workers due to differences in interpretation of measurements.

For most of the current work reported here, it was necessary to use KNUDSEN cell mass spectrometry for determining bond energies of the high-temperature molecules we had been studying because only few of these had previously been known, i.e. characterized by optical spectroscopy, and most of these molecules were present in very minor concentrations, typically 10^{-2} to 10^{-6} of that of the predominant species.

The method and its principle results have been described in a number of reviews[1-5], and references to these reviews and other papers quoted therein is made. A critical examination of the limitations in applying mass spectrometry to high-temperature equilibrium studies has recently been presented[6].

We shall immediately proceed to present some of our results and compare them with relevant published data. Where appropriate, the measured bond energies will be discussed in terms of empirical models which also have proven useful for predicting bond energies of not yet known related molecules. These are, the PAULING model of a polar bond[7] and the model of constant ratio between dissociation energy of a molecule and heat of atomization of the corresponding condensed phase with the same formula[8].

A large part of the experimental work was performed with a mass spectrometer at the Battelle Memorial Institute. Current work is being performed at Texas A and M University. Some experiments had been carried out with an instrument at the University of Rome.

Selected Results and Discussion

1. *Molecular Metals*

A large portion of our work in recent years has been devoted to the determination of bond energies of molecular metals and intermetallic compounds with emphasis on diatomic molecules. Among the purposes of this work were the extension and refinement of the PAULING model[7] and, in applying this model, a possible refinement of the PAULING electronegativity scale.

According to this model, the bond energy, $D(A-B)$, of a diatomic molecule, AB, may be expressed by the relation:

* Lecture given on Dezember 21, 1971 at the Chemical Institute of the University of Zurich.

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[6] F. E. STAFFORD, *High Temp. – High Press. 3* (1971) 213.
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$$D(A{-}B) = 1/2\ [D(A{-}A) + D(B{-}B)] + 23\,(\chi_A{-}\chi_B)^2 \quad \text{(in kcal mol}^{-1}\text{)},$$

where $D(A{-}A)$ and $D(B{-}B)$ are "single bond energies" of component elements A and B, respectively, and χ_A and χ_B are the respective electronegativities on the PAULING scale[7]. The first term gives the covalent contribution to the bond energy $D(A{-}B)$, to which the ionic resonance contribution, expressed by the second term, is added. This arithmetic mean version of the model is most commonly used. The alternate "geometric mean version" is given by $D(A{-}B) = [D(A{-}A) \times D(B{-}B)]^{1/2} + 30\,(\chi_A{-}\chi_B)^2$ (in kcal mol^{-1}). The necessary single bond energies for the non-metals are given by PAULING[7]. A set of single bond energies for all non-transition elements has been calculated by SANDERSON[9]. No single bond energies are available for transition metals. Here the experimental dissociation energies may be used when applying the PAULING model for bond energy calculations. Recent reviews of dissociation energies of diatomic metals and intermetallic compounds have been given by SIEGEL[10], DROWART[11], GAYDON[12] and GINGERICH[5].

It is obvious that if the dissociation energy of a homonuclear, diatomic, transition-element molecule can be determined, the PAULING model can be applied to many heteronuclear, diatomic compounds of this metal. Thus, part of our emphasis has been to determine previously unknown dissociation energies of transition metals. In order to test the applicability of the PAULING model we have focussed on intermetallic compounds for which the electronegativity differences of the component atoms are relatively large. Thus the expected ionic resonance contribution is large and a sensitive test of the model is possible. For this reason, we have concentrated our efforts on the investigation of intermetallic rare earth compounds with gold.

Table I. Experimental and calculated bond energies of some gaseous rare earth aurides. Values are in kcal mol^{-1}

(See text for further explanation)

M	χ(M)[a]	D(M—M)	D(M—Au) Experimental	D(M—Au) Calculated
Sc	1.4	38.0 ± 5[b]	66.1 ± 4[e]	69
Y	1.3	37.3 ± 5[b]	71.1 ± 4[e]	73
La	1.3	57.6 ± 5[b]	79.5 ± 5[a]	78
Ce	1.3	57.0 ± 4[a]	77.0 ± 3.5[a]	78
Pr	1.3	(37)[a]	72.0 ± 5[a]	(71)
Nd	1.3	(32)[a]	70.6 ± 5[a]	(69)
Tb	1.3	34 ± 8[c]	67 ± 5[c]	71,5
Ho	1.3	19.0 ± 4[d]	60.5 ± 4[c,d]	64
Lu	1.3	33 ± 8[c]	78.5 ± 4[c]	71

[a] Reference 13
[b] Reference 5
[c] Reference 16
[d] Reference 14
[e] Reference 15

Table II. Calculated bond energies of selected diatomic intermetallic compounds with copper using the PAULING model[a] and comparision with experimental values (all in kcal mol^{-1})

M	χ_M[b]	D(M—M)[c]	$\bar{D}$(M—Cu) Co-valent	$\bar{D}$(M—Cu) Ionic	D(M—Cu) Calculated	D(M—Cu) Experimental[c]
Ti	1.3	32 ± 5	38.5	11.3	49.8	
V	1.3	57 ± 4	51.0	11.3	62.3	
Cr	1.4	36 ± 7	40.5	8.3	48.8	
Mn	1.4	10 ± 7	27.5	8.3	35.8	37.0 ± 4[f]
Fe	1.7	29 ± 5	37.0	2.1	39.1	
Co	1.7	39 ± 6	42.0	2.1	44.1	37.8 ± 4[f]
Ni	1.8	52.5 ± 5	48.7	0.9	49.6	48.3 ± 4[f]
Pd	2.0	25 ± 5	35.0	0.0	35.0	
Ag	1.9	38 ± 1.5	41.5	0.2	41.7	40.7 ± 2.2
Au	2.3	53.0 ± 1.5	49.0	2.1	51.1	55.3 ± 2.2
Al	1.4	40.6 ± 3.5[d]	42.5	8.3	50.8	50.0 ± 3.0[d]
Ga	1.5	33.0 ± 2.0	39.0	5.7	44.7	
In	1.6	24 ± 2	34.5	3.7	38.2	
Sn	1.6	45.8 ± 4	45.4	3.7	49.1	41.4 ± 4
Sn	1.6	34.2[e]	39.6	3.7	43.3	41.4 ± 4
Pb	1.6	20 ± 5	32.5	3.7	36.2	

[a] Using $D(M{-}Cu) = 1/2[D(M{-}M) + D(Cu{-}Cu)] + 23\,(\chi_M{-}\chi_{Cu})^2$ kcal mol^{-1} with $D(Cu{-}Cu) = 45.0 \pm 1.5$ kcal mol^{-1}[c] and $\chi_{Cu} = 2.0$[b]
[b] PAULING electronegativities corrected for valence state
[c] Reference 5
[d] Considering Reference 17 in addition to Reference 5
[e] Single bond energy, Reference 7
[f] Reference 18

A summary of the results is presented in Table I, along with the bond energies calculated according to the PAULING model and the D(M—M) and χ_M values on which the calculations were based. To obtain the best fit for the molecules LaAu and CeAu[13], the value $\chi_M = 1.3$ was used for Y and the lanthanides, in preference to the values (1.1 to 1.2) given by PAULING. Accordingly, χ_{Sc} of 1.4 rather than 1.3[7] was applied. Except for LuAu, the agreement between experimental and calculated values is very good. This agreement can in turn be taken as support for the choice of the electronegativities of the rare earth elements.

In principle, one can use the model to calculate bond energies of many binary metal compounds. This is exemplified in Table II for selected copper-metal compounds for which the electronegativity differences are not as large as for the rare earth aurides. For many of these experimental values are available, which are listed for comparison. Inspection of Table II shows that agreement between experimental and calculated values is good, except for CoCu. Even in this case it is reasonably good when one considers the rather large uncertainty in the experimental value for the dissociation energy of Co_2. Since the ionic contribution is very small for this molecule the small discrepancy may be attributed to a deviation of the covalent contribution rather than a deviation from the model. It is also noteworthy that a better agreement is obtained in the case of SnCu, if the single bond energy is used for D(Sn—Sn)[7] instead of the experimental dissociation energy. One could convenient-

ly add calculated values for rare earth intermetallic compounds with copper. Their measurement would lead to a better test of the PAULING model than is provided by the experimental data known to this date, due to the larger electronegativity difference and accompanying larger ionic contribution to the bond energy.

Recently we have measured the atomization energies for the first polyatomic intermetallic compounds, namely $LuAu_2$, $HoAu_2$, and $TbAu_2$[16]. The values suggest symmetric molecules, AuMAu with an average energy per bond that is comparable to the bond energy of the corresponding diatomic M—Au molecule. The results are summarized in Table III. They indicate that the PAULING model can be applied to such polyatomic intermetallic compounds, and gives good agreement with the average bond energy per bond. On the basis of these results we expect the PAULING model also to apply to diaurides of other rare earth metals and of the actinides.

Table III. Comparison of the experimental and calculated bond energies of diatomic and triatomic metal-aurides (in kcal mol^{-1})[a]

M	D(M—Au) Calculated	D(M—Au) Experimental	$1/2D(MAu_2)$ Experimental	MAu_2
Lu	71	78.5 ± 4	72.0 ± 4	$LuAu_2$
Ho	64	60.5 ± 4	65.5 ± 4	$HoAu_2$
Tb	71.5	66.8 ± 4	71.6 ± 4	$TbAu_2$

[a] Reference 16

It is also of interest to consider where the PAULING model fails. It is not expected to apply to molecules constituted of non-metals, where multiple bonding is known to occur. According to BREWER[19], multiple bonding is also expected for gaseous intermetallic compounds for which the corresponding condensed systems form very stable compounds. This particularly applies to combinations between electropositive transition metals with empty *d*-orbitals, such as the group III, IV, or V transition metals, the lanthanides, and actinides, and elements that contain almost filled *d*-shells, such as the platinum group metals. By transferring one or more of the paired electrons from the platinum group metal atoms to the *d*-electron deficient transition metal atom more valence electrons on both atoms become available for bonding, thus favoring a bond order higher than one. A qualitative confirmation of this expectation has been provided by spark source mass spectrometric experiments, in which apparently very stable molecules between platinum metals and group IV transition metals were formed[20]. Subsequent KNUDSEN cell mass spectrometric experiments yielded exceptionally stable molecules, such as LuPt ($D_0^0 = 95 \pm 8$ kcal mol^{-1})[21], CePd ($D_0^0 = 76.1 \pm 4$ kcal mol^{-1})[22], and TiRh ($D_0^0 = 88.9 \pm 5$ kcal mol^{-1})[23]. In the latter two instances, the corresponding bond energies calculated after the PAULING model are 60 kcal mol^{-1} for both, CePd and TiRh. Clearly, the experimental values are markedly higher, indicating a bond order larger than one, in support of the applicability of the BREWER-ENGEL metallic theory to gaseous intermetallic compounds. Thus a large group of intermetallic compounds may be expected to form stronger bonds than predicted by the PAULING model. Optical spectroscopic measurements on such molecules in addition to bond energy determinations and molecular orbital considerations may throw more light on the nature of the bonding in these molecules.

Another class of intermetallic compounds for which the PAULING model may not apply is the group of compounds formed from copper subgroup elements with alkali metals or alkali earth metals. Already for alkali or alkali earth hydrides the bond energies found are lower than those calculated according to the PAULING model, but this fact has been attributed to electronegativity differences of 1.5 or larger, in which case the model usually no longer applies[7]. So far the bond energy has been measured for only one of these compounds, namely NaAg, and found to be equal to the arithmetic mean of the dissociation energies of the component metals within the accuracy of measurement[24]. Clearly, the PAULING model does not apply in this case.

2. *Molecules Containing Non-metals*

The KNUDSEN cell mass spectrometric method has also been found very suitable for the determination of the enthalpies of high temperature equilibria involving new molecules that contain non-metallic elements. From the experimental reaction enthalpies, dissociation and atomization energies for these molecules have been derived. Examples from our laboratory concern mainly molecules which occur in minor concentrations only and for which the method appears to be the only one available for the experimental determination of bond energies. For correlating the measured bond energies, the concept of a

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Table IV. Calculated bond energies of some gaseous rare earth pnictides[a]

Metal M	χ(M) Literature	D(M—M)	D(M—P)[b] Calculated	D(M—As)[b] values	D(M—Sb)[b]
Sc	1.4	38.0 ± 5	56	43	40
Y	1.3	37.3 ± 5	59	46	42
La	1.3	57.6 ± 5	66	56	52
Ce	1.3	57.0 ± 4	65	56	52
Ho	1.3	19.0 ± 4	46	38	33

[a] After PAULING: $D(M—X) = 1/2[D(M—M) + D(X—X)] + 23(\chi_M—\chi_X)^2$, in kcal mol^{-1}
[b] With $D(X—X)$: P = 51.3; As = 32.1; Sb = 30.2 in kcal mol^{-1} and χ_X: P = 2.1; As = 2.0; Sb = 1.9

constant α-parameter[8], has been useful and has been illustrated for application to diatomic metal nitrides[5]. The fact that isoelectronic molecules frequently have similar atomization energies and the observation that in the formation of triatomic molecules the average bond energies from the binary component molecules are transferable to the ternary molecule is also noted. Reference to examples has been made elsewhere[5].

With respect to the PAULING model, indications that it applies to certain diatomic metal nitrides[5], carbides[25] and borides[26] have been discussed elsewhere. It can also be applied to polyatomic molecules, such as metal dicarbides[25], diborides[27], and cyanides or isocyanides[28], if one treats the C_2, B_2 or CN radical as a pseudo atom to which a certain electronegativity can be assigned. One may also expect that the model will apply to pnictides other than nitrides, and to illustrate this point the calculated values for some of the rare earth phosphides, arsenides, and antimonides are shown in Table IV. To test the model further we plan to study some of these molecules. The calculated values for the dissociation energies indicate that these molecules are expected to play a very minor role in the vapor over the corresponding condensed phases, and that high ion detection sensitivity will be required for their measurement.

Finally the estimation of the dissociation energy of the AlN molecule from the comparison of the recently determined dissociation energy of gaseous BP[29] with the literature values for the dissociation energies of other molecules isoelectronic with BP is illustrated. For these molecules, the PAULING model does not seem to be applicable, either because of multiple bond formation (e.g. SiC) or because of too large an electronegativity difference between the component atoms (e.g. NaF). It is, however, interesting to note (Table V) that pairs of isoelectronic molecules between members of the same family have, within the accuracy of knowledge, the same dissociation energy, e.g. LiCl and NaF; and BeS and MgO. This holds, despite of the rather large electronegativity difference for the component atoms in each molecule of either pair. Extending this analogy to the corresponding pair BP and AlN, the dissociation energy of the latter has been estimated as 85 ± 10 kcal mol^{-1}.

Table V. Comparison of the dissociation energies of boron monophosphide and isoelectronic molecules

Molecule	D_0^0(AB) kcal mol^{-1}	Molecule AB	D_0^0(AB) kcal mol^{-1}
LiCl	113 ± 3[a]	AlN	70 ± 23[a]
NaF	114 ± 7[a]		87 ± 20[c]
BeS	88 ± 14[a]		82 — 137[d]
MgO	94 ± 14[a]		85 ± 10[b]
BP	82 ± 4[b]	SiC	103 ± 5[a]

[a] Reference 12
[b] Reference 29
[c] Reference 30
[d] Reference 31

Other previous estimates for D(AlN), which were based on estimated molecular parameters[12,30] and on ionic model calculations[31], are also shown in Table V.

Conclusions

The presented examples for bond energy measurements of small molecules by high temperature mass spectrometry were intended to illustrate the power of this method, especially when applied to molecules that constitute only a small fraction of the equilibrium vapor. Under such conditions the high sensitivity and consequent large dynamic range of the method, together with the possibility to measure partial pressures of all vapor species present, make it superior to any other method presently available. Furthermore for reactions which involving major species, and thus permitting measurements over a very large temperature range, excellent second law reaction enthalpies can be obtained which are as accurate as is possible by any other thermochemical method.

The correlation of results with empirical models of bonding has been illustrated so extensively, because the new data obtained permit the extension and refinement of these models and thus increase their predicting power. This is of theoretical interest as well as of practical interest when measuring new systems and molecules.

It is somewhat surprising that the application of this method to the determination of bond energies of small high temperature molecules has actually diminished

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since its high during the first decade. This is accentuated because the knowledge of bond energies of new molecules is also expected to stimulate optical spectroscopic studies of molecular parameters of such molecules in the gas phase and when isolated in a solid inert matrix at very low temperatures. For the smallest molecules the experimental bond energies will also permit to test and thus accelerate the development of, *ab initio* calculations of bond energies. This may lead to a more rapid practical replacement of empirical theories of bonding such as the PAULING model by more fundamental theories with yet greater and more accurate predicting power.

Acknowledgements

It is a pleasure to acknowledge the kind invitations of Professors OSWALD and VISCONTINI to present this lecture in Switzerland. The author also expresses his appreciation for the support of the preparation of the manuscript by the Robert A. Welch Foundation under Grant A-387, and for Grant GP-31 863 by the National Science Foundation to assist in defraying the transportation expenses.