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Dissociation energies of BaI and CaI from equilibrium studies

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Effusion-beam mass spectrometry was used to study the gaseous dissociation equilibrium $\text{BaI} = \text{Ba} + \text{I}$ and the isomolecular exchange reactions of BaI and CaI with ScI over wide temperature ranges, and thermochemical data were derived from second law analysis. The results yielded the dissociation energies $D_0^\circ(\text{BaI}) = 76.2 \pm 1.5 \text{ kcal mol}^{-1}$ and $D_0^\circ(\text{CaI}) = 67.0 \pm 2 \text{ kcal mol}^{-1}$. Both of these values are about 5 kcal mol^{-1} larger than previous results obtained in this laboratory from third law analysis of other reactions. Reasons for the disparities are discussed. Our new second result for BaI is in good agreement with a recent value obtained from crossed molecular beam studies.

I. INTRODUCTION

From energy-balance considerations in the analysis of the crossed molecular beam reaction



Zare and co-workers¹ were able recently to set a firm lower bound to the dissociation energy (D_0°) of BaI, obtaining $D_0^\circ(\text{BaI}) \leq 76.8 \pm 1.7 \text{ kcal mol}^{-1}$. By combining this result with an earlier upper bound $D_0^\circ(\text{BaI}) \leq 78.5 \pm 0.5 \text{ kcal mol}^{-1}$ based on predissociation studies,² they recommended $D_0^\circ(\text{BaI}) = 77.7 \pm 2 \text{ kcal mol}^{-1}$ as the present best value. Other determinations of $D_0^\circ(\text{BaI})$ were discussed,¹ including an equilibrium value of $71.4 \pm 1.0 \text{ kcal mol}^{-1}$ obtained previously in our laboratory by mass spectrometry.³ Because it was possible to characterize accurately the internal state distributions of reagents and products, the latter by laser spectroscopy, Zare and co-workers¹ concluded that the equilibrium value³ $D_0^\circ(\text{BaI}) = 71.4 \text{ kcal mol}^{-1}$ was incompatible with the degree of vibrational excitation observed in product BaI.

Chemical bond strengths, typified by $D_0^\circ(\text{BaI})$, are critical physical quantities that are as yet accessible only by experiment when accuracies of $\sim 2 \text{ kcal mol}^{-1}$ or better are required. It is important, therefore, for testing theories of chemical bonding and for refining detailed molecular energy calculations that disparities in the literature are resolved. We recently had occasion to reexamine the thermochemistry of $\text{BaI}(g)$ for other reasons and indeed found that our earlier equilibrium value³ appears to be low by about 5 kcal mol^{-1} . Our previous determination was based on third law analysis of an isomolecular exchange reaction with the reference partner GaI and also of the gaseous reaction $\text{Ba} + \text{BaI}_2 = 2 \text{ BaI}$. In order to avoid possible uncertainties in the properties of reference species such as GaI and BaI_2 , we chose instead to study the dissociation equilibrium



and to derive the desired reaction enthalpy change (equivalent to the dissociation energy) from second law analysis. Because of uncertainties in evaluating absolute reaction equilibrium constants from mass spectrometric measurements and related uncertainties in the spectroscopic con-

stants needed for third law analysis, we have focused recently on the second law approach as a more reliable alternative.

In addition, second law studies of the isomolecular exchange reactions of BaI and CaI with ScI gave thermochemical results supporting the new value from reaction (2), while also showing that our earlier equilibrium data³ gave a similarly high value for $D_0^\circ(\text{CaI})$. These new mass spectrometric-equilibrium results on BaI and CaI are presented here.

II. EXPERIMENT

Equilibrium mixtures of the gaseous species of interest were generated in a heated effusive beam source and were monitored by mass spectrometry. The BaI, Ba, and I species were generated by reaction of $\text{BaO}(s)$ with $\text{I}_2(g)$ in a molybdenum effusion cell with gas inlet; I_2 vapor was generated by vaporization of the solid from an external container at room temperature, and the flow was controlled with a precision leak valve. The Ba-Sc-I and Ca-Sc-I species were produced in tandem molybdenum effusion cells with elemental Sc in the upper chamber and $\text{BaI}_2(s)$ or $\text{CaI}_2(s)$ in the lower. Cell temperatures were measured with a calibrated optical pyrometer, sighting on a black body cavity in the lid.

The magnetic-sector mass spectrometer system and the related experimental technique have been described previously.^{3,4} In the equilibrium measurements, all measured ion signals were checked with the beam-defining slit to eliminate potential background contributions. Gaseous species were identified from the masses, threshold appearance potentials, and isotopic spectra of the ions produced by electron impact; appearance potentials were evaluated by the vanishing current method. The accuracy of second law slope determinations is checked regularly by measurements on vapor pressure standards such as gold; experimental errors associated with such measurements and the estimated uncertainties in derived thermochemical results have been discussed earlier.⁵

The $\text{BaO}(s)$, $\text{BaI}_2(s)$, $\text{CaI}_2(s)$, $\text{Sc}(s)$, and $\text{I}_2(s)$ samples were all reagent grade materials obtained from commercial suppliers. No further characterization was required, since only gaseous equilibria were studied and no significant impurities were noted in the mass spectra.

III. RESULTS

Threshold appearance potentials (AP) of the ion species generated by the reactions $\text{BaO}(s) + \text{I}_2(g)$, $\text{BaI}_2(g) + \text{Sc}(s)$, and $\text{CaI}_2(g) + \text{Sc}(s)$ at about 1600 K are listed in Table I. The magnitude of the AP's confirm that all ions are parent ions, formed by simple ionization of the corresponding neutrals. Thus, the metal monoiodides BaI, CaI, and ScI, and the atomic species Ba, Ca, Sc, and I are present in the cell beams with the appropriate samples; their partial pressures were monitored without fragmentation interference by measurement of the parent ion intensities at electron energies of 3 eV above the respective thresholds. For the isomolecular reactions, equilibrium constants, K , were evaluated from the parent ion ratios without further correction; for reaction (2), a pressure calibration based on the vapor pressure of gold was used in estimating the absolute value of K from the measured intensities. In the thermochemical analysis of the equilibrium data, thermal functions for gaseous Ba, Ca, I, BaI, and CaI are from Chase *et al.*⁶ while functions for Sc are from Hultgren *et al.*⁷ and those of ScI from Hildenbrand *et al.*⁸

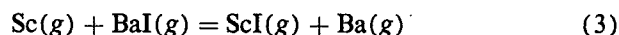
With the $\text{BaO}(s) + \text{I}_2(g)$ effusive source, the reaction equilibrium (2) was studied over the range 1571 to 1777 K and the derived equilibrium constants K are listed in Table II. Also included are the coefficients in the expression $\log K = A + B/T$ determined from least-squares fitting; the stated uncertainties are standard deviations, measures of precision only. Second law analysis yielded the slope enthalpy change $\Delta H_{1661}^\circ(2) = 78.0 \pm 1.5 \text{ kcal mol}^{-1}$, which is converted to $\Delta H_0^\circ(2) = 76.2 \pm 1.5 \text{ kcal mol}^{-1}$ with the aid of thermal functions. The corresponding third law value at 0 K is $74.4 \pm 2.5 \text{ kcal mol}^{-1}$, where the uncertainty reflects mainly a potential error of a factor of 2 in the derived equilibrium constant. Agreement between second and third law values is reasonable. However, the second law analysis requires only a quantity proportional to K (rather than the absolute value) and is felt to be inherently more reliable for equilibria of this type if systematic errors in temperature measurement and control can be minimized. The preferred second law enthalpy change is equivalent to the dissociation energy $D_0^\circ(\text{BaI}) = 76.2 \pm 1.5 \text{ kcal mol}^{-1}$.

An alternate value for $D_0^\circ(\text{BaI})$ can be derived from measurements of the equilibrium

TABLE II. Equilibrium data for the reaction $\text{BaI}(g) = \text{Ba}(g) + \text{I}(g)$ (2).

T/K	$K_2 \times 10^7$ (atm)
1571	3.16
1571	3.28
1596	5.08
1596	4.98
1596	4.90
1596	4.95
1624	7.35
1673	14.7
1673	14.9
1709	23.2
1709	24.6
1709	23.5
1744	40.5
1777	60.6
1777	63.3

$\log K_2$ (atm) = $(4.373 \pm 0.090) - (17\,054 \pm 149)/T$



made with the $\text{Sc}(s) + \text{BaI}_2(g)$ source. In Table III are listed values of K for reaction (3) calculated from the parent ion ratios at temperatures of 1458 to 1683 K. Least-squares fitting gave the second law enthalpy change $\Delta H_{1584}^\circ(3) = 10.1 \pm 1.5 \text{ kcal mol}^{-1}$, which is corrected to $\Delta H_0^\circ(3) = 8.5 \pm 1.5 \text{ kcal mol}^{-1}$ with the aid of thermal functions noted above. Combination of this result with $D_0^\circ(\text{ScI}) = 69.2 \pm 1.5 \text{ kcal mol}^{-1}$ from the recent literature⁸ gives $D_0^\circ(\text{BaI}) = 77.7 \pm 2.1 \text{ kcal mol}^{-1}$, thereby corroborating the more direct, preferred value from reaction (2).

TABLE III. Equilibrium data for the reaction $\text{Sc}(g) + \text{BaI}(g) = \text{ScI}(g) + \text{Ba}(g)$ (3).

T/K	$K_3 \times 10^2$
1458	2.16
1503	2.24
1503	2.39
1529	2.46
1529	2.58
1545	2.63
1545	2.59
1562	2.59
1562	2.69
1575	2.84
1584	3.07
1584	3.08
1584	3.05
1601	2.99
1601	2.87
1613	3.12
1621	3.12
1621	3.01
1647	3.31
1651	3.17
1651	3.20
1683	3.26
1683	3.32

$\log K_3 = -(0.151 \pm 0.096) - (2210 \pm 151)/T$

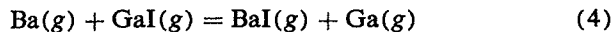
TABLE I. Threshold appearance potentials and neutral precursors of observed ion species.

Ion	Appearance potential, eV ^a	Neutral
Ba ⁺	5.0	Ba
BaI ⁺	5.0	BaI
Ca ⁺	6.0	Ca
CaI ⁺	6.1	CaI
Sc ⁺	6.6	Sc
ScI ⁺	6.5	ScI
I ⁺	10.5	I

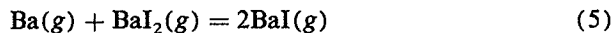
^aUncertainty ± 0.3 eV.

Third law calculations on reactions involving ScI are considerably more uncertain because of the unknown electronic state contributions.

Our selected value $D_0^\circ(\text{BaI}) = 76.2 \pm 1.5 \text{ kcal mol}^{-1}$ is 4.8 kcal mol⁻¹ higher than an earlier mass spectrometric value from this laboratory³ based on third law analysis of the equilibria

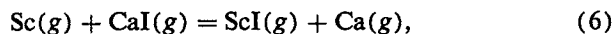


and

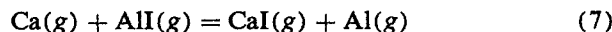


generated by the reaction of a BaO(s)–Ga₂O₃(s) mixture with HI(g). The value of $D_0^\circ(\text{BaI})$ reported here, however, is in accord with the recent result of Zare and co-workers,¹ $D_0^\circ(\text{BaI}) = 77.7 \pm 2 \text{ kcal mol}^{-1}$, derived from crossed molecular beam studies combined with laser spectroscopy.

Similar measurements of the equilibrium



with the Sc(s) + CaI₂(g) source gave the K values shown in Table IV and the second law value $\Delta H_{1585}^\circ(6) = -0.5 \pm 1.5 \text{ kcal mol}^{-1}$ and $\Delta H_0^\circ(6) = -2.2 \pm 1.5 \text{ kcal mol}^{-1}$. Combination with $D_0^\circ(\text{ScI})$ (Ref. 8) gives $D_0^\circ(\text{CaI}) = 67.0 \pm 2.1 \text{ kcal mol}^{-1}$, which is 4.9 kcal mol⁻¹ higher than the value reported earlier³ from mass spectrometric studies of the equilibrium



based on third law analysis.

TABLE IV. Equilibrium data for the reaction $\text{Sc}(g) + \text{CaI}(g) = \text{ScI}(g) + \text{Ca}(g)$ (6).

T/K	K_6
1472	1.25
1479	1.32
1479	1.32
1496	1.17
1496	1.21
1513	1.32
1513	1.32
1529	1.26
1553	1.32
1553	1.35
1574	1.27
1574	1.29
1575	1.24
1591	1.34
1591	1.19
1591	1.30
1591	1.24
1594	1.33
1594	1.25
1604	1.28
1656	1.15
1687	1.23
1687	1.28
1709	1.24
1753	1.28
1753	1.24

$\log K_6 = (0.030 \pm 0.072) + (115 \pm 112)/T$

TABLE V. Summary of reaction thermochemistry.

Gaseous reaction	ΔH_0° kcal mol ⁻¹	Selected value kcal mol ⁻¹
BaI = Ba + I	76.2 ± 1.5	$D_0^\circ(\text{BaI}) = 76.2 \pm 1.5$
Sc + BaI = ScI + Ba	8.5 ± 2	
Sc + CaI = ScI + Ca	-2.2 ± 2	$D_0^\circ(\text{CaI}) = 67.0 \pm 2$

A summary of the reaction thermochemistry and the selected dissociation energies from this study is given in Table V.

IV. DISCUSSION

Although it seems clear now that the previous³ mass spectrometric values for $D_0^\circ(\text{BaI})$ and $D_0^\circ(\text{CaI})$ are both too low by about 5 kcal mol⁻¹, the reasons for this disparity are not obvious. The earlier results³ on BaI were based primarily on third law analysis of reaction (4), which indicated $D_0^\circ(\text{GaI}) - D_0^\circ(\text{BaI}) \cong 10 \text{ kcal mol}^{-1}$; the reference value for $D_0^\circ(\text{GaI})$ used at that time, $82.0 \pm 1 \text{ kcal mol}^{-1}$, has been corroborated in recent studies⁸ that gave $D_0^\circ(\text{GaI}) = 80.2 \pm 1.5 \text{ kcal mol}^{-1}$, so that the GaI data are not at fault. The earlier data³ were also supported by third law analysis of reaction (5), but significant fragmentation corrections were required for BaI₂. It seems more likely that some combination of factors involving noncancellation of cross sections and perhaps incorrect fragmentation assumptions gave somewhat erroneous equilibrium constants that affected third law calculations. A factor of five error in K , which is larger than normally expected but probably not out of range, could account for the difference. On the whole, experience has led us to prefer accurate second law measurements whenever possible.

For CaI, the earlier determination³ was based solely on the monoiodide exchange reaction with AlI which yielded $D_0^\circ(\text{AlI}) - D_0^\circ(\text{CaI}) = 23 \text{ kcal mol}^{-1}$ and $D_0^\circ(\text{CaI}) = 62.1 \pm 2.5 \text{ kcal mol}^{-1}$. However, $D_0^\circ(\text{AlI})$ has not been firmly established; the previously adopted value of 85.0 kcal mol⁻¹ is 2 kcal mol⁻¹ lower than a spectroscopic value⁹ and could account for part of the discrepancy between new and older values for $D_0^\circ(\text{CaI})$. Uncertainties in the measured K values, as discussed above, could also have affected the third law calculations.

In any event, we believe that the new second results on BaI and CaI are more reliable and should clearly supersede the earlier third law values.³ In particular, the BaI dissociation equilibrium data, i.e., from reaction (3), are strongly preferred because no reference partner with its inherent thermochemical uncertainties is required in deriving $D_0^\circ(\text{BaI})$. It is also especially satisfying that the new BaI data agree well with the crossed molecular-beam results¹ on reaction (1), in which laser spectroscopy was used to probe the internal state distributions in product BaI, thereby increasing the accuracy of the energy-balance considerations.

ACKNOWLEDGMENT

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