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## Dissociation energy of the molecule AIBr from equilibrium measurements

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The dissociation equilibrium AlBr = Al + Br was studied by effusion beam mass spectrometry over the range 1970 to 2260 K and the dissociation energy  $D_0^0$  (AlBr) was derived as  $4.41 \pm 0.06$  eV. This value is in general agreement with other fragmentary thermochemical results, but it is lower than a value derived from a short extrapolation of vibrational levels in the excited  ${}^{1}\pi$  state, doubtless because of a potential maximum of about 0.22 eV in that state. A Birge-Sponer extrapolation of the ground state vibrational levels, when corrected for degree of ionicity, yields a  $D_0^0$  value in close accord with the experimental result, but an electrostatic model calculation falls short by 0.45 eV.

#### INTRODUCTION

The boron-aluminum group monohalide molecules have closed-shell valence electronic structures and are relatively stable high temperature species. They can be readily generated in molecular beams or flowing gas streams by interaction of the metal and metal trihalide phases, or by reduction of the trihalides, and many have now been accurately characterized by optical, microwave, and photoelectron spectroscopic techniques, as well as by mass spectrometry. For the aluminum monohalides, the spectroscopic and molecular constants are well established, and a number of electronic transitions involving the  $1\pi$  and  $3\pi$  upper states and the  $1\Sigma$  ground state have been observed and analyzed.

The  ${}^{1}\pi$  states of these molecules all have rather shallow potential curves that can be reliably extrapolated to an apparent dissociation limit, thus providing a spectroscopic route to the ground state dissociation energies  $D_{0}^{0}$  since the electronic energies  $T_{e}$  of the states and excitation energies of the products are well established. Barrow<sup>1</sup> has discussed the upper state extrapolation procedure and has derived  $D_{0}^{0}$  values for all of the boron, aluminum, gallium, indium, and thallium monohalides by this method.

However, as pointed out by Barrow,<sup>1</sup> there is always the possibility of maxima in upper state potential curves because of interference due to avoided crossing of curves of the same electronic species. An upper state extrapolation may therefore yield the vibrational energy at the top of the maximum, rather than at the true dissociation limit, and the derived  $D_0^0$  value will be too large. Barrow<sup>1</sup> has shown strong evidence for maxima in the  ${}^1\pi$  states of AlF and AlCl by comparing spectroscopic and thermochemical dissociation energies, and this has been corroborated by Murad *et al.*<sup>2</sup> for the  ${}^1\pi$  states of BF, GaF, InF, and TlF with barrier heights *h* ranging from 0.22 to 0.34 eV.

For AlBr, the evidence is less conclusive because the thermochemical  $D_0^0$  is not well established. Semenkovich<sup>3</sup> reported an equilibrium pressure for the process

$$Al(1) + NaBr(1) = AlBr(g) + Na(g)$$
(1)

at a single temperature (1175 K) and the results were used to derive  $D_0^0$  (AlBr).<sup>4</sup> However, there is some question about the actual vapor composition and the properties of the condensed phase.<sup>3</sup> The JANAF Tables also list unpublished measurements on the equilibrium

$$2/3Al(1) + 1/3AlBr_3(g) = AlBr(g)$$
 (2)

by Gross and colleagues.<sup>5</sup> From an analysis of these two studies,<sup>3,5</sup> the JANAF Tables<sup>4</sup> selected  $D_0^0$  (AlBr) = 4.37 ± 0.13 eV. In another critical review,<sup>6</sup> these results<sup>3,5</sup> were reevaluated and combined with unpublished measurements by Gorokhov and co-workers<sup>7</sup> on the reaction

$$Al(g) + NaBr(g) = AlBr(g) + Na(g)$$
(3)

to give  $D_0^0(AlBr) = 4.48 \pm 0.06$  eV. Since there is an uncertainty of at least 0.1 eV in  $D_0^0(AlBr)$  and much of the work is problematical and/or unpublished, we carried out new thermochemical studies of  $D_0^0(AlBr)$  to get a more accurate measure of the potential maximum h in the  $1\pi$  state, if one exists. A secondary goal was to carefully characterize a diatomic metal bromide that could be used as a reference partner in gaseous equilibrium studies of other metal bromides.

Our new results on AlBr, obtained by effusion-beam mass spectrometry, help to resolve these conflicting values and the details are presented here.

#### **EXPERIMENTAL**

An effusion beam containing the species to be studied was generated by the reaction of gaseous  $Br_2$  with  $Al_2O_3(s)$ in a molybdenum cell. The Br<sub>2</sub> was admitted to the cell from an external reservoir and its flow controlled with a molecular leak valve. Monitoring of beam composition and pressure as a function of cell temperature was done by mass spectrometry in a direct sampling mode, using the magnetic sector instrument and experimental technique described in earlier publications.<sup>8,9</sup> Following our customary procedure, parent ion signals were measured a few eV above ionization threshold to eliminate fragmentation effects that tend to obscure the neutral precursors of observed ion species. All measured signals were subjected to the beam-defining slit test to ascertain their effusion cell origin. The instrument was operated with a mass resolution of about 700, which was sufficient to fully resolve all observed mass peaks. Cell temperatures were measured by optical pyrometry, sighting on a black-body cavity in the lid.

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The powdered  $Al_2O_3$  sample was "ultra pure" 99.995% material from ROC/RIC, while the  $Br_2$  was analytical reagent grade material from Mallinckrodt.

#### RESULTS

At temperatures above 1900 K, the neutral species Al, Br, and AlBr were observed in the effusion beam generated by reaction of  $Br_2$  with  $Al_2O_3$ . In addition to exhibiting the proper mass and isotopic distribution, the Al<sup>+</sup>, Br<sup>+</sup>, and AlBr<sup>+</sup> signals had threshold appearance potentials of 5.8, 11.9, and 9.1 eV, respectively, in accord with expected values for the neutral parents. These values were determined by the vanishing current method, and have uncertainties of 0.3 eV. The spectroscopic ionization potentials (IP) of Al and Br are 5.986 and 11.814 eV, respectively,<sup>10</sup> and a threshold of 9.3 eV has been previously reported for AlBr.<sup>11</sup> Our threshold value of 9.1 + 0.3 eV for AlBr is in line with those of AlF (9.73 eV)<sup>12</sup> and AlCl (9.4 eV),<sup>11</sup> showing the expected decrease with changing halogen orbital character. Since IP  $(AlBr)-IP(Al) \sim 3 eV$ , the electron removed on ionization of AlBr is clearly a bonding electron, and the dissociation energy of the molecular ion AlBr<sup>+</sup> will be smaller than that of the neutral by  $\sim 3 \text{ eV}$ .

In any event, the ionization threshold measurements clearly established the presence of the species Al, Br, and AlBr in the effusing beam above 1900 K and that there were no interfering fragment contributions to the parent ion signals within a few eV of threshold. A series of measurements of the dissociation equilibrium

$$AlBr(g) = Al(g) + Br(g)$$
(4)

was then made by measuring the corresponding parent ion intensities at 3 eV above their respective ionization thresholds, for a number of temperatures in the range 1974 to 2262 K. Although the major emphasis of this work was on accurate determination of the temperature dependence of the equilibrium constant  $K_{eq}$  of reaction (4), which does not require absolute values (second law method), a pressure calibration based on the vapor pressure of gold was used to determine the instrument sensitivity constant so that  $K_{eq}$ could be evaluated and third law calculations could be checked for consistency. Values of  $K_{eq}$  for reaction (4) obtained in this way are summarized in Table I, along with second and third law enthalpy changes derived from the results. Substantial changes in species intensities, induced by varying the Br<sub>2</sub> flow rate, had no effect on derived values of  $K_{eq}$ , showing that chemical equilibrium was attained.

The second law (II) enthalpy change  $\Delta H_{2123}^{\circ}(4) = 438.1 \pm 6.3$  kJ mol<sup>-1</sup> was derived by least squares fitting of the data in Table I; the stated uncertainty of 6.3 kJ mol<sup>-1</sup> is believed to include errors from all sources (including systematic errors), while the uncertainty of 2.6 kJ mol<sup>-1</sup> derived from the coefficient of the equilibrium constant expression in Table I is the statistical standard deviation reflecting precision only. This value can be converted to standard reference temperature with the aid of thermal functions from the JANAF Tables,<sup>4</sup> yielding  $\Delta H_{298}^{\circ}(4) = 429.3 \pm 6.3$ kJ mol<sup>-1</sup>. From the absolute value of  $K_{eq}$ , one derives the average third law (III) enthalpy change  $\Delta H_{298}^{\circ}(4) = 425.5$ 

TABLE I. Derived thermodynamic data for the gaseous reaction AlBr = Al + Br.

T	K×10 <sup>6</sup>	$\Delta H^{\circ}_{298}$ (III)
( <b>K</b> )	(atm)	(kJ/mol)
1974	1.64	425.9
1974	1.67	425.9
1974	1.61	426.4
2037	3.98	425.1
2037	3.78	425.9
2079	6.31	425.9
2086	6.99	425.5
2086	7.06	425.5
2171	19.2	425.1
2199	26.2	425.1
2199	25.5	425.5
2243	38.2	426.8
2263	51.9	424.7
2263	48.6	425.9
2263	50.7	425.1
	Average	425.5
	$\Delta H_{298}^{\circ}$ (II)	$429.3 \pm 6.3$
	$\log K (\text{atm}) = (5.814 \pm 0.063) - (22884)$	$\pm 136)/T$

 $\pm$  12 kJ mol<sup>-1</sup>, in close accord with the second law result; the error limit in the third law value derives from a factor of 2 estimated uncertainty in the reaction equilibrium constant. We believe that the second law value is inherently more reliable and use it in deriving the dissociation energy  $\Delta H_0^0 = D_0^0 (\text{AlBr}) = 425.9 \pm 6 \text{ kJ mol}^{-1} = 4.41 \pm 0.06$ eV. Our new value for  $D_0^0$  (AlBr) lies between the earlier selected values  $4.37 + 0.13 \text{ eV}^4$  and 4.48 + 0.06 eV,<sup>6</sup> but it has the advantage of involving a complete series of measurements over a large temperature range and being fully documented. The new result for  $D_0^0$  (AlBr) also agrees closely with that listed by Huber and Herzberg,<sup>13</sup> 4.43 eV, but the latter stems from an early analysis by Barrow<sup>14</sup> of the aforementioned measurement by Semenkovich,<sup>3</sup> and is subject to revision with changes in auxiliary data. Because it is a direct thermochemical measurement of the dissociation equilibrium, the present determination of  $D_0^0$  (AlBr) is independent of the heat of sublimation of Al, which itself is uncertain by 0.04 eV.4

### DISCUSSION

It seems clear that  $D_0^0$  (AlBr) is now well established at  $4.41 \pm 0.06$  eV. From a short extrapolation of vibrational levels in the  $A^{-1}\pi$  state, Barrow<sup>1</sup> derived  $D_0^0$  (AlBr) =  $4.63_6$  eV, while the highest observed vibrational level indicated  $D_0^0 \ge 4.53$  eV and a predissociation limit led to  $D_0^0 \le 4.58$  eV. All of this points to a potential maximum *h* of about 0.22 eV in the  $^{1}\pi$  state of AlBr, similar to those found in AlF (0.35 eV) and AlCl (0.26 eV).<sup>1,13</sup> Interestingly enough, the evidence is strong that no maxima are present in the  $^{1}\pi$  states of InCl and TlCl.<sup>1,15</sup>

From purely theoretical calculations, Langhoff *et al.*<sup>16</sup> suggest that the thermochemical value  $D_0^0$  (AlBr) = 4.43 eV<sup>13</sup> is low, and that the correct value is closer to the predissociation limit of 4.56 eV. Further, they<sup>16</sup> suggest that a potential barrier of 0.35 eV in the  $A^{1}\pi$  state of AlF is much too high, with the calculations indicating h = 0.05 eV. By implication, the maxima in AlCl and AlBr should be even smaller, a point clearly at odds with the thermochemical results. Although the power of the theoretical calculations is quite impressive, the comparison with experiment indicates that in this instance, at least, the calculated  $D_0^0$  values are likely to be uncertain by 0.1 to 0.2 eV, depending on the corrections applied. This is nevertheless an exceptional standard of reliability, and more widespread application of molecular theory would certainly be welcome.

A linear Birge-Sponer extrapolation (LBX) of the ground state vibrational levels of AlBr yields  $D_0^0$  (LBX) = 3.43 eV, as calculated from the established spectroscopic constants<sup>13</sup>  $\omega_e$  and  $\omega_e x_e$  by the relation

$$D_0^0(\text{LBX}) = (\omega_e^2/4\,\omega_e x_e) - 1/2\omega_e.$$
 (2)

It is well recognized that  $D_0^0$  (LBX) tends to be too large for relatively covalent diatomics, and too small for highly ionic molecules, because of the substantially different vibrational potential functions for these two extreme cases, and the resulting variation in convergence rate of the levels at large internuclear separation. It has been suggested, however, that a reasonable correction can be applied to  $D_0^0$  (LBX), based on the ionicity parameter  $r_x/r_e$ , where  $r_x$  is the hypothetical crossing point of ionic and covalent potential curves, and  $r_e$ is the equilibrium internuclear distance.<sup>17</sup> Application of this ionicity correction<sup>17</sup> yields a revised  $D_0^0$  (LBX), of 4.40 eV, in fortuitously close agreement with experiment, but indicative that the approach is valid.

With  $r_x/r_e = 2.39$ , AlBr has a relatively high degree of ionic character and should be susceptible to an electrostatic model calculation of  $D_0^{0.17}$  The same is true of AlF and AlCl which are more highly ionic, with  $r_x/r_e$  values of 3.44 and 2.84, respectively. The chief difficulty here is in specifying the dipole polarizability  $\alpha$  of the monovalent ion Al<sup>+</sup> needed in the calculation.<sup>17</sup> Since the free ion Al<sup>+</sup> cannot be readily studied, only an estimate of  $\alpha(Al^+)$  is available. Using methods outlined earlier,<sup>8</sup>  $\alpha(Al^+)$  was estimated to be  $2.4 \times 10^{-3}$  nm<sup>3</sup> (2.4 Å<sup>3</sup>). Taking AlF as a test case, and with all atomic and molecular data from standard sources,<sup>4,13</sup> we calculate  $D_0^0$  (AlF) = 6.68 eV from the Rittner electrostatic model<sup>17</sup> with  $\alpha = 2.4 \times 10^{-3}$  nm<sup>3</sup>. This initial calculated  $D_0^0$  (AlF) is only 0.21 eV lower than the experimental value,<sup>13</sup> suggesting that the estimated  $\alpha$  is reasonable. Increasing  $\alpha$  (Al<sup>+</sup>) slightly to  $3.0 \times 10^{-3}$  nm<sup>3</sup> gives essentially complete agreement between experiment and the ionic model calculation of  $D_0^0$  (AlF). Extending the ionic model to AlCl and AlBr with  $\alpha$ (Al<sup>+</sup>) =  $3.0 \times 10^{-3}$  nm<sup>3</sup>, we calculate  $D_0^0$  (AlCl) = 4.52 eV and  $D_0^0$  (AlBr) = 3.96 eV, lower than the experimental values by 0.60 and 0.45 eV, respectively. Judging from the AlF case, one might expect better agreement, but the model does have limitations and pushing to the less-ionic chlorides and bromides may be unwarranted.

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- <sup>1</sup>R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960).
- <sup>2</sup>E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. 45, 263 (1966).
- <sup>3</sup>S. A. Semenkovich, Zh. Prikl. Khim. 30, 933 (1957).
- <sup>4</sup>JANAF Thermochemical Tables, J. Phys. Chem. Ref. Data 14, Suppl. No. 1 (1985).
- <sup>5</sup>P. Gross, Fulmer Research Institute (unpublished data).
- <sup>6</sup>Thermodynamic Properties of Individual Substances, Institute for High Temperatures, Academy of Sciences, U.S.S.R., Vol. III (1981).
- <sup>7</sup>L. N. Gorokhov, Institute for High Temperatures, U.S.S.R. (unpublished data).
- <sup>8</sup>D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968); 52, 5751 (1970); 65, 614 (1976).
- <sup>9</sup>K. H. Lau and D. L. Hildenbrand, J. Chem. Phys. 71, 1572 (1979).
- <sup>10</sup>C. E. Moore, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. No. 34 (U.S. GPO, Washington, D.C., 1970).
- <sup>11</sup>D. L. Hildenbrand, J. Chem. Phys. 66, 3526 (1977).
- <sup>12</sup>J. M. Dyke, C. Kirby, A. Morris, B. W. J. Gravenor, R. Klein, and P. Rosmus, Chem. Phys. 88, 289 (1984).
- <sup>13</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- <sup>14</sup>R. F. Barrow, Nature 189, 480 (1961).
- <sup>15</sup>J. Berkowitz and T. A. Walter, J. Chem. Phys. 49, 1184 (1968).
- <sup>16</sup>S. R. Langhoff, C. W. Bauschlicher, Jr., and P. R. Taylor, J. Chem. Phys. 88, 5715 (1988).
- <sup>17</sup>D. L. Hildenbrand, J. Electrochem. Soc. **126**, 1396 (1979).