

DETERMINATION OF $D_0^\circ(\text{BaI})$ FROM THE CHEMILUMINESCENT REACTION $\text{Ba} + \text{I}_2$

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A study is made of the visible chemiluminescence resulting from the reaction of an atomic beam of barium with I_2 under single-collision conditions ($\sim 10^{-4}$ torr). The resulting spectrum consists of the $\text{BaI } C^2\Pi \rightarrow X^2\Sigma$ emission on top of an underlying "continuum". The variation of the BaI emission intensity with Ba and I_2 flux is investigated, and it is concluded that the reaction is bimolecular. The total phenomenological cross section for barium atom removal is determined to be 86 \AA^2 , which agrees well with the total reactive cross section calculated assuming an electron jump mechanism. The short wavelength cutoff is identified as the transition from the $v' = 41$ level of the $\text{BaI } C^2\Pi_{3/2}$ state to the $v'' = 41$ level of the $\text{BaI } X^2\Sigma$ state. A strict lower bound $D_0^\circ(\text{BaI}) \geq 102 \pm 0.7$ kcal/mole for the ground state dissociation energy of BaI is obtained from this short wavelength cutoff. The value $D_0^\circ(\text{BaI}) = 102 \pm 1$ kcal/mole is recommended, where the error estimate includes the possible contribution from the final relative translational energy of the products.

1. Introduction

The bond energy of BaI is not well known. Gaydon [1], in his most recent compilation of bond energies, regards the experimental data as too unreliable to permit him to recommend a value for $D_0^\circ(\text{BaI})$. The previous best estimate has been the ionic model calculation of Krasnov and Karaseva [2] who give $D_0^\circ(\text{BaI}) = 85 \pm 15$ kcal/mole. Most recently, Mims, Lin and Herm [3] set a lower limit on $D_0^\circ(\text{BaI})$ of 66 kcal/mole from their observed product angular distribution data for the crossed beam reaction of Ba with HI. Chemiluminescent reactions under single-collision conditions offer a new means of setting lower bounds to dissociation energies [4-10]. A preliminary analysis by Gole [11] of the $\text{Ba} + \text{IBr}$ reaction yielded the bound $D_0^\circ(\text{BaI}) \geq 97$ kcal/mole. We report here a study of the chemiluminescent reaction $\text{Ba} + \text{I}_2$, which has been undertaken to provide a reliable estimate of the ground state BaI bond strength.

The determination of thermodynamic properties for high-temperature species is always welcome because such data is sparse. The ground state dissociation energy of BaI is needed because it permits one to calculate the energetics of gas-phase reactions of Ba with iodine-containing compounds. Recently, there is special inter-

est in the reaction systems $\text{Ba} + \text{HI}$ [3, 12], $\text{Ba} + \text{CH}_3\text{I}$ [13], and $\text{Ba} + \text{CH}_2\text{I}_2$ [13], because the BaI reaction product can be detected by laser-induced fluorescence. This has motivated us to make a determination of $D_0^\circ(\text{BaI})$.

2. Experimental

The beam apparatus, LABSTAR, has been previously described [8, 9]. It consists of a water-cooled Astro-oven (Astro Industries, Inc.) which resistively heats a cylindrical graphite tube containing a cylindrical graphite crucible with an aperture of 0.1 cm in diameter. The entire crucible-heater arrangement is surrounded by three concentric tantalum heat shields. The barium (99.9% purity and obtained from Atomergic Chemetal Co.) is heated until the vapor pressure inside the crucible reaches 0.1 torr. Under these conditions, the beam flux in the reaction zone is estimated to be $\lesssim 10^{16}$ atoms $\text{cm}^2 \text{ s}^{-1}$. The iodine (99.99% purity and obtained from J.T. Baker Chemical Co.) is heated inside a pyrex tube wrapped with nichrome wire connected to a Variac. The I_2 pressure is regulated with a teflon stopcock attached to the pyrex tube. No provisions are made to

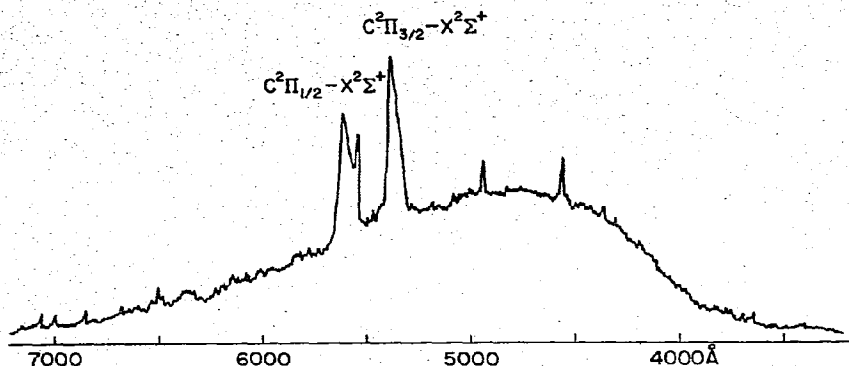


Fig. 1. The Ba + I₂ chemiluminescent spectrum taken at a scan rate of 500 Å/min and 5 Å resolution. The BaI C²Π → X²Σ emission occurs on top of the underlying continuum. Ba emission lines are also present.

collimate the iodine beam, and it essentially fills the entire reaction chamber (beam + gas arrangement). At low iodine pressures (10⁻⁵ to 10⁻⁴ torr) the chemiluminescent reaction is produced by single collisions. The pressure is measured with an ionization gauge located near the reaction zone. However, the reactivity of the iodine may affect the accuracy of the pressure readings.

The chemiluminescence is detected with a 1 meter Interactive Technology Czerny—Turner spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. A cooled Centronic S-20 photomultiplier is attached to the exit slits of the spectrometer. The photomultiplier signal serves as the input to a Keithley 417 fast picoammeter whose output drives a Hewlett—Packard 7100B strip-chart recorder. All spectra are uncorrected for the variation of detector response with wavelength.

3. Appearance of the spectra

Fig. 1 shows a rapid scan at 500 Å/min and 5 Å resolution of the chemiluminescent spectrum for the reaction of Ba with I₂. The spectrum consists of the BaI* C²Π_{3/2, 1/2}—X²Σ⁺ emission and an underlying continuum as observed in the beam-gas chemiluminescent spectra for other Ba + X₂ reactions [15, 16]. Fig. 2 shows a slow scan at 10 Å/min and 1 Å resolution of the short wavelength portion of the BaI C²Π_{3/2}—X²Σ⁺

band system. Sequential members of the vibrational progression move in the direction of shorter wavelengths. The overlapping of rotational structure obscures the clarity of the bandheads, which are more prominent in the Ba + I₂ spectra obtained in the presence of argon at 4 torr [17]. However, the sharp cut-off at the (41,41) transition can be identified. The

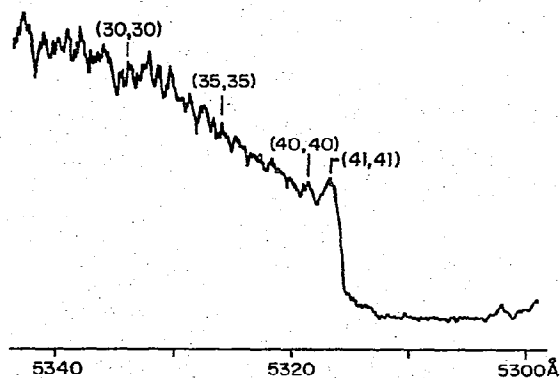


Fig. 2. The short wavelength portion of the chemiluminescent spectrum for the reaction Ba + I₂ → BaI* + I taken at a scan rate of 10 Å/min and 1 Å resolution. The temperature of the Ba oven is 1220 K and the I₂ pressure is 8 × 10⁻⁴ torr. At I₂ pressures below 2 × 10⁻⁴ torr, this cutoff appears as a rapid change in the slope of the emission in this wavelength region. At higher I₂ pressures, the (41,41) transition is readily identified at the sharp cutoff.

bandhead assignments are based on the work of Patel and Shah [18]. At pressures of $\approx 10^{-5}$ torr to 1×10^{-4} torr, the cutoff appears as a sharp change in the slope of the emission in this wavelength region. It is this sharp, short wavelength cutoff that is important for the determination of the BaI dissociation energy. It should be noted that this cutoff is not caused by pre-dissociation or pre-ionization in the excited state, since higher (v' , v'') bands have been seen by Patel and Shah in emission.

4. Reaction molecularity and kinetics

For a bimolecular reaction of barium with iodine the chemiluminescent intensity will be proportional to the concentration of both barium and iodine, i.e.,

$$I \propto [\text{Ba}] [\text{I}_2]. \quad (1)$$

The barium atom concentration is proportional to the vapor pressure of barium inside the effusive oven. With increasing oven temperature, the vapor pressure, P , of the barium increases according to the Clausius-Clapeyron relation

$$d \ln P / d(1/T) = -\Delta H_T / R, \quad (2)$$

where ΔH_T is the latent heat of vaporization at the temperature T (taken to be the mean of the temperature range investigated). The iodine concentration is proportional to the I_2 pressure in the scattering chamber. Thus, the reaction molecularity is determined by monitoring the chemiluminescent intensity as a function of oven temperature and I_2 pressure.

We have studied the chemiluminescent intensity at a fixed oxidant pressure and at a fixed wavelength when the oven temperature is varied. A typical plot of the logarithm of the chemiluminescent intensity vs the reciprocal of the oven temperature is presented in fig. 3. We conclude from the linearity of the plot that the reaction of barium with iodine is first order in the barium flux. The slope of the straight line gives the latent heat of vaporization for barium, provided the reaction rate does not change appreciably with velocity (temperature). We obtain from an average of five measurements in the temperature range 1100 to 1250 K

$$\Delta H_{1175} = 45 \pm 3 \text{ kcal/mole}. \quad (3)$$

This is in good agreement with the published values of

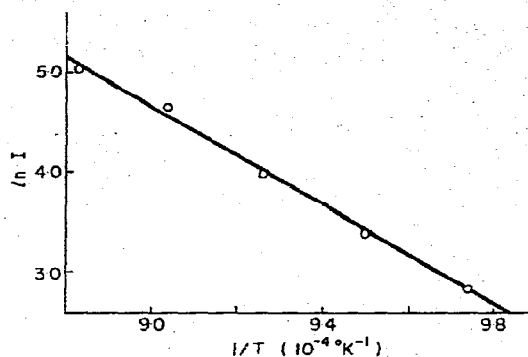


Fig. 3. A typical plot of the logarithm of the chemiluminescent intensity as a function of $1/T$ at a fixed I_2 pressure of 4×10^{-4} torr and a fixed wavelength of 5380 Å. The linearity of the plot shows that the reaction $\text{Ba} + \text{I}_2 \rightarrow \text{BaI}^* + \text{I}$ is first order in Ba flux. The slope indicates that the reaction takes place with ground state Ba.

42 kcal/mole obtained by Parshina and Kortuneko [19] and 46 kcal/mole obtained by Nesmeyanov [20].

The intensity of the chemiluminescence at a fixed wavelength and fixed oven temperature is studied as a function of iodine pressure. The linearity of the plot given in fig. 4 also shows that the chemiluminescent intensity is proportional to the iodine flux. Since the reaction is first order in both the Ba and I_2 flux, the chemi-

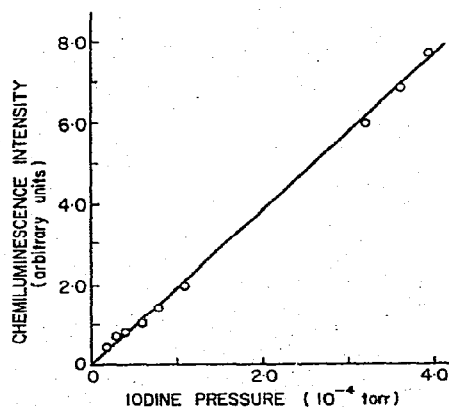


Fig. 4. A plot of the chemiluminescent intensity as a function of I_2 pressure at a fixed Ba oven temperature of 1220 K and a fixed wavelength of 5380 Å. The linearity of this plot shows that the reaction $\text{Ba} + \text{I}_2 \rightarrow \text{BaI}^* + \text{I}$ is first order in I_2 flux.

luminescent reaction proceeds by a simple bimolecular mechanism involving the collision of a ground state Ba atom with an I_2 molecule.

At higher iodine pressure, the linear plot of fig. 4 reaches a maximum at $\approx 8 \times 10^{-4}$ torr and turns downward with increasing pressure (see fig. 5). This reflects the attenuation of the barium beam between the entrance port of the reaction chamber and the reaction zone viewed by the spectrometer. If the chemiluminescent intensity is assumed to obey a $p \exp(-\alpha p)$ relationship where p is the oxidant pressure, an upper limit to the reaction cross section can be determined. The linear term in p describes the formation of excited state molecules and the exponential term describes the attenuation of the barium beam by the iodine. The attenuation parameter α in torr^{-1} is related to the total phenomenological cross section for barium atom removal, σ , in \AA^2 by

$$\alpha = 1.33 \times 10^{-13} l \sigma / kT, \quad (4)$$

where l is the beam path length (4.5 cm) in the reaction chamber from the port of entry to the reaction zone viewed by the spectrometer, k is Boltzmann's constant in erg K^{-1} , and T is the absolute temperature (≈ 300 K for iodine). The constant 1.33×10^{-13} has units of $\text{dyne torr}^{-1} \text{\AA}^2$. The maximum in the plot of I vs p occurs at

$$p_{\max} = 1/\alpha. \quad (5)$$

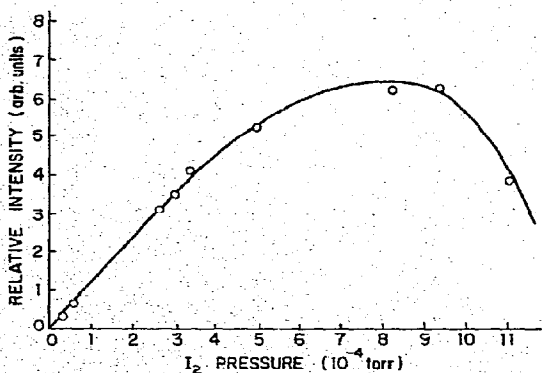


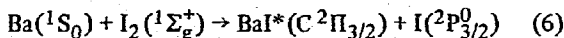
Fig. 5. A plot of the chemiluminescent intensity as a function of higher I_2 pressures at a fixed Ba oven temperature of 1220 K and a fixed wavelength of 5380 Å. The maximum occurs approximately at 8×10^{-4} torr.

Thus, the attenuation parameter can be estimated from the intensity maximum ($\sim 8 \times 10^{-4}$ torr); then σ is determined by eq. (4). The total phenomenological cross section comprising all attenuation effects for the reaction of barium with iodine is 86\AA^2 . It should be noted that any error in pressure caused by the reactivity of iodine with the ionization gauge will be strongly reflected in this result. Hence, this upper bound to the total reaction cross section should be regarded as a crude estimate.

Assuming an electron jump mechanism, a crossover radius of 5.5 Å can be calculated using 5.2 eV for the ionization potential of Ba [21] and 2.6 eV for the vertical electron affinity of I_2 [22]. This radius gives a geometric cross section (πr_c^2) of 94\AA^2 for the reaction of Ba with I_2 , which agrees with the total cross section determined above (86\AA^2). This upper bound to the total reaction cross section represents the production of mostly ground state BaI molecules since the photon yield reported at pressures of 4 torr of argon is less than 4% for the $\text{Ba} + I_2$ reaction [17].

5. Dissociation energy of BaI

For chemiluminescent reactions that proceed by a bimolecular mechanism, it is possible to determine a lower bound to the bond dissociation energy of the diatomic product. From the application of energy balance to the reaction



and neglecting the final relative translational energy, the inequality

$$D_0^o(\text{BaI}) \geq D_0^o(I_2) + E_{\text{int}}(\text{BaI}) - E_{\text{int}}(I_2) - E_{\text{trans}}^i \quad (7)$$

provides a lower bound to $D_0^o(\text{BaI})$. The average internal energies of I_2 and BaI, $E_{\text{int}}(I_2)$ and $E_{\text{int}}(\text{BaI})$, are measured from their lowest energy levels. The initial relative translational energy, E_{trans}^i , is measured in the center-of-mass frame. The dissociation energy of I_2 is taken to be $12440.9 \pm 1.1 \text{ cm}^{-1}$ (35.571 ± 0.003 kcal/mole) [23].

The internal energy of the iodine includes both rotational and vibrational contributions. The rotational contribution is simply $RT = 209 \text{ cm}^{-1}$. The vibrational contribution to the internal energy of I_2 is determined by the average thermal distribution of the ground

state vibrational levels, i.e.,

$$\bar{E}(v) = \frac{\sum_v G(v) \exp \{-[G(v) - G(0)]/kT\}}{\sum_v \exp \{-[G(v) - G(0)]/kT\}} \quad (8)$$

Using the $G(v)$ values for iodine [24] and summing to $v=4$ (where the vibrational population decreases to 2% of that at $v=0$), the vibrational contribution to $E_{\text{int}}(\text{I}_2)$ is 222 cm^{-1} . The total rotational and vibrational contribution to the internal energy of I_2 is $E_{\text{int}}(\text{I}_2) = 431 \text{ cm}^{-1}$ (1.23 kcal/mole).

The initial relative translational energy is estimated from the expression [25]

$$E_{\text{trans}}^i = \frac{3}{2} kT_{\text{eff}} \quad (9)$$

where

$$T_{\text{eff}} = \frac{T(\text{Ba})m(\text{I}_2) + T(\text{I}_2)m(\text{Ba})}{m(\text{I}_2) + m(\text{Ba})} \quad (10)$$

Here $T(\text{Ba}) = 1220 \text{ K}$, $T(\text{I}_2) = 300 \text{ K}$, $m(\text{Ba}) = 2.28 \times 10^{-22} \text{ g}$, and $m(\text{I}_2) = 4.22 \times 10^{-22} \text{ g}$, yielding $E_{\text{trans}}^i = 2.67 \text{ kcal/mole}$.

The internal energy of BaI is found from the short wavelength cutoff of the chemiluminescent spectrum, the (41, 41) band head of the $\text{C}^2\Pi_{3/2} - \text{X}^2\Sigma^+$ transition. The internal energy of BaI can then be found from either of the following expressions:

$$E_{\text{int}}(\text{BaI}) = T_{00}(\text{C}^2\Pi_{3/2}) + G'(41) - G'(0), \quad (11)$$

and

$$E_{\text{int}}(\text{BaI}) = E_{\text{swco}} + G''(41) - G''(0). \quad (12)$$

Here $G(v)$ and T_{00} have their traditional meanings [26] and E_{swco} is the energy corresponding to the short wavelength cutoff. The calculational procedure is illustrated in fig. 6. We use the molecular constants for BaI based on the reanalysis [13] of the band head positions of Patel and Shah [18]. For the $\text{C}^2\Pi_{3/2}$ state we have $T_{00}(\text{C}^2\Pi_{3/2}) = 18\,571.56 \text{ cm}^{-1}$, $\omega_e' = 158.153 \text{ cm}^{-1}$ and $\omega_e x_e' = 0.2748 \text{ cm}^{-1}$, where the vibrational dependence of the spin-orbit constant has been incorporated into the effective vibrational constant ω_e' . For the $\text{X}^2\Sigma^+$ state we have $\omega_e'' = 152.299 \text{ cm}^{-1}$ and $\omega_e x_e'' = 0.2703 \text{ cm}^{-1}$. Using these values in eq. (10) and eq. (11), $E_{\text{int}}(\text{BaI})$ is $24\,582.6 \text{ cm}^{-1}$ (70.29 kcal/mole) and $24\,585.2 \text{ cm}^{-1}$ (70.29 kcal/mole), respectively.

The dissociation energy of BaI is now determined from eq. (6) to be

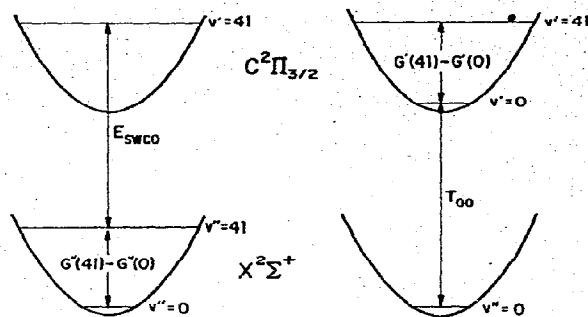


Fig. 6. The determination of $E_{\text{int}}(\text{BaI})$ is accomplished by (a) using the short wavelength cutoff E_{swco} or (b) using the T_{00} value of the BaI $\text{C}^2\Pi_{3/2}$ state. The exact transition which populates the highest vibrational level in the excited state, in this case the (41, 41) transition, must be known for both methods.

$$D_0^0(\text{BaI}) \geq 102.0 \pm 0.7 \text{ kcal/mole} \quad (13)$$

The initial relative translational energy distribution for the Ba + I_2 reaction in a beam-gas arrangement is expected to have a broad distribution. This large spread is the main source of error in determining $D_0^0(\text{BaI})$. Care must be taken since collisions with Ba atoms having large E_{trans}^i may be the mechanism for populating the highest observed BaI internal states. An estimate of the error associated with E_{trans}^i is $\pm 0.6 \text{ kcal/mole}$. Similarly, higher vibrational levels in ground state I_2 may be responsible for populating the highest BaI internal states. A very conservative estimate of this error is $\pm 0.3 \text{ kcal/mole}$. The uncertainty in the determination of $E_{\text{int}}(\text{BaI})$ is only $\pm 0.05 \text{ kcal/mole}$ and that for $D_0^0(\text{I}_2)$ is only $\pm 0.003 \text{ kcal/mole}$. The final error estimate assumes that all the above errors are independent.

The value for $D_0^0(\text{BaI})$ is a lower bound in eq. (13) because the final relative translational energy of the products E_{trans}^f is neglected. Specifically, we need the value of E_{trans}^f that applies to the products when BaI is in its highest internal state. The next higher vibrational level, $v'' = 42$, lies only 134 cm^{-1} (0.38 kcal/mole) above $v'' = 41$, yet it is not populated. Since the energy in this reaction is released early in the approach of the reactants, it is reasonable that the partitioning of the reaction energy does not correspond to some

fixed fraction appearing in product translational energy. Hence, we suggest that the final relative product translational energy of BaI($C^2\Pi_{3/2}, v' = 41$) and I($^2P_{3/2}$) is close to zero, on the average. Consequently, we take

$$D_0^{\circ}(\text{BaI}) = 102 \pm 1 \text{ kcal/mole} \quad (14)$$

as the ground state dissociation energy of the BaI molecule, where the error estimate reflects the possible contribution of E_{trans}^f .

Acknowledgement

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