FORMATION OF GROUP IIA DIHALIDES
BY TWO-BODY RADIATIVE ASSOCIATION ‡

C. D. JONAH and R. N. ZARE

Department of Chemistry, Columbia University,
*New York, New York, USA*

. Chemiluminescence from crossed beams of group IIA metal atoms (M) and halogen molecules (X_2) is observed. and evidence is presented for the reaction $M + X_2 \rightarrow MX_2^* \rightarrow MX_2 + h\nu$. Lower limits to the dissociation energy of BaCl and SrCl are placed at 110 kcal/mole and 99 kcal/mole. respectively. and the cross section for the formation of BaCl is estimated to be 60 $Å^2$.

Using the technique of crossed-beam chemiluminescence [1], we have studied the reactions of group IIA metal atoms with halogen molecules. In particular, we have examined the reaction Ba + Cl_2 under single-collision conditions. A barium beam ($\approx 10^{15}$ atoms/sec) effusing from an oven enters a differentially pumped chamber, where it collides with Cl_2 gas (≈ 0.2 millitorr). The resulting chemiluminescence is collected and focused on the entrance slits of a 3/4-m Czerny-Turner spectrometer. A recorder tracing of the spectrum is shown in fig. 1. The principal conclusions of this experiment are: (1) the major source of chemiluminescent light is the two-body radiative association process

$$Ba + Cl_2 \rightarrow BaCl_2^* + h\nu \;;$$
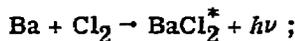
(2) a minor source of chemiluminescent light is the reaction

$$Ba + Cl_2 \rightarrow BaCl^* + Cl \rightarrow BaCl + Cl + h\nu \,,$$

from which a lower limit of $D_0^0 = 110$ kcal/mole is placed on the BaCl dissociation energy; (3) the Ba-resonance line 6s6p $^1P^0 - 6s^2$ ^1S appears but is second order in the Ba pressure; (4) we estimate that the value of the total reactive cross section is 60 $Å^2$, and we attribute the cross section primarily to the reaction

$$Ba + Cl_2 \rightarrow BaCl^\dagger + Cl \,,$$
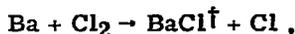
where BaCl† is a vibrationally excited BaCl molecule in the ground electronic state. Similar conclusions are also drawn from our studies of the chemiluminescent reaction Sr + Cl_2.
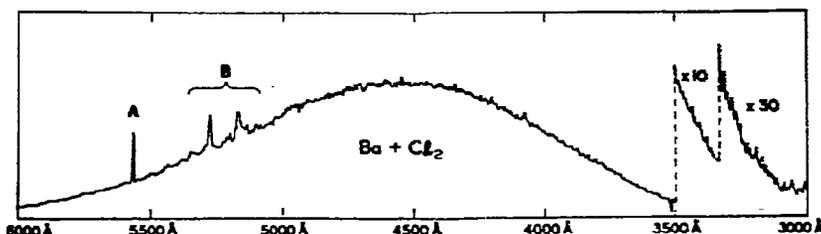
Fig. 1. Spectrum of chemiluminescence from the reaction Ba + Cl_2: The letter A represents the 6s6p $^1P^0 - 6s^2$ ^1S Ba-resonance line and the letter B represents the BaCl-emission bands (the $^2\Pi - ^2\Sigma$ green system). The featureless emission from 2900 to 6000 Å is assigned to emission from an excited electronic state of $BaCl_2$.

If two collision partners A and B come together on an excited potential surface, they may form the AB molecule by two-body radiative association (recombination), provided that an electronic transition takes place to the ground state during their collision time [2]. Since typical collision times are usually much less than molecular radiative lifetimes, two-body radiative association is normally regarded as a rare event. The experimental evidence concerning this process is scant, since the presence of three-body recombination as well as the possible participation of molecular dimers has often complicated the interpretation of these experiments ‡.

The most prominent feature in fig. 1 is a structureless emission band which we shall refer to as an "emission continuum". In fig. 2 we present the experimental data from which we have concluded that the emission continuum is linear in both the Cl_2 and Ba pressures, and hence results from two-body radiative association. Fig. 2a shows a plot of the intensity of the emission continuum as a function of Cl_2 pres-
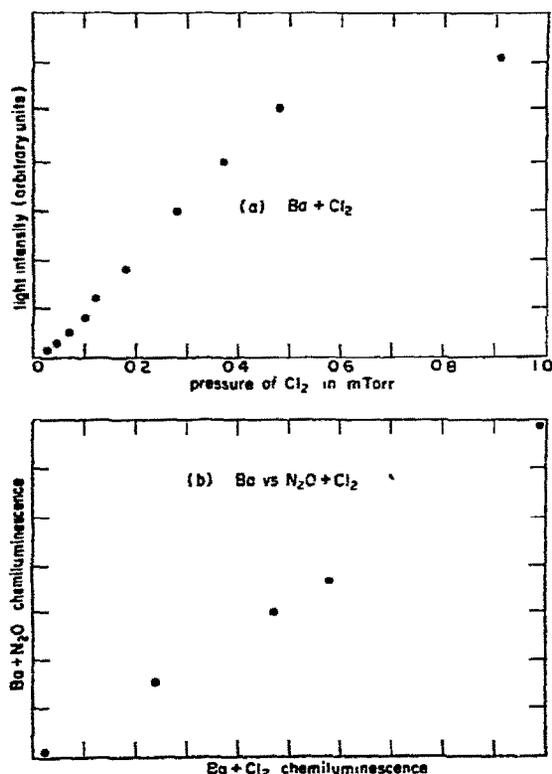
sure; fig. 2b shows a plot of the intensity of the chemiluminescent light resulting from the reaction Ba + NO_2 against the intensity of the continuum emission from the reaction Ba + Cl_2. From previous studies of the Ba + NO_2 reaction [1], it can be inferred that this reaction is first order in both the Ba and the NO_2 pressures. Hence, figs. 2a and 2b taken together demonstrate that the origin of the emission continuum is a bimolecular reaction involving Ba and Cl_2.

Note that the emission continuum peaks at 4500 Å and trails off into the noise at 2900 Å (4.1 eV). The dissociation energy of Cl_2 is 57.2 kcal/mole (2.5 eV) [4]. Thus the species responsible for the emission continuum must result from a highly exothermic reaction yielding a product that requires an energy of 6.6 eV or more to separate the product into its constituent atoms. This is consistent with the supposition that $BaCl_2$ is the emitter, since the D_0^0 value for $BaCl_2$ [equal to D_0^0 (ClBa - Cl) + D_0^0 (BaCl)] has been determined to be about 9.4 eV [5].

A model for the formation of $BaCl_2$ from Ba + Cl_2 must account for the greater likelihood of this reaction occurring. An electron jump can take place at large distances in such a manner that the $BaCl_2$ system crosses over from a covalent potential surface dissociating into Ba + Cl_2 to an ionic surface dissociating into Ba^+ + Cl_2^-. As the two species approach each other on the Ba^+ + Cl_2^- potential surface, the Cl atoms draw apart, and more charge flows from the central Ba atom to each peripheral Cl atom. This causes the molecule to execute complex Lissajous motion about the equilibrium structure:

$$Ba^{+(2-2\delta)} \diagdown^{Cl^{-(1-\delta)}}_{Cl^{-(1-\delta)}}$$
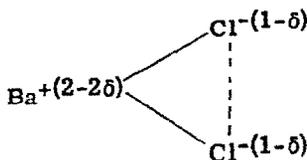
where $0 < \delta < 1$. The ground state of $BaCl_2$ is known to be bent [6], and simple calculations predict that the excited state is also nonlinear [7]. Accordingly, once the above conformation has been reached, concerted motion of the two Cl atoms is required for them to return their

Fig. 2. Pressure dependence of continuum emission for the reaction Ba + Cl_2 (see text).

‡ The best known example of two-body radiative association is the airglow reaction, NO + O → NO_2. This has been most recently studied by Becker et al. [3] who were able to separate the two-body and three-body contributions to the formation of NO_2^*.

charge to the central Ba atom and to depart through the entrance channel whence they came. As a consequence of the phase space associated with the bent $BaCl_2^*$ structure, this molecular complex is expected to be long-lived, thus enhancing the probability for two-body radiative association. In the patois of molecular beamists and other whaling enthusiasts, this model may be described as " a harpoon mechanism followed by a gaffing reaction to accomplish the coup de grace".

In the language of spectroscopy, this process is the inverse of molecular predissociation [2]. Because of the high density of states of the $BaCl_2^*$ complex, the vibrational-rotational structure of the emission would not be observed with a spectrometer of our resolution. It follows from the Franck-Condon principle that inverse predissociation would produce preferentially $BaCl_2$ ground-state molecules having high vibrational and rotational excitation. Hence, it would be expected that not all the the energy of reaction appears as chemiluminescence. This mechanism also explains the continuum emission we have observed in the chemiluminescence from $Sr + Cl_2$. Moreover, the mechanism of two-body radiative association should also be applicable to the formation of other group IIA dihalides and may be applicable to the formation of other metal halides.

As is characteristic of all high-temperature species, dissociation-energy determinations of metal halides are fraught with experimental difficulties. By observing the short-wavelength limit $(h\nu)_{SW}$ of the BaCl and SrCl chemiluminescence, we are able to place a lower bound on the dissociation energies $D_0^0(MCl)$ of these species. From the conservation of energy it follows that we should have the condition.

$$D_0^0(MCl) \geqslant D_0^0(Cl_2) + (h\nu)_{SW} - \epsilon_R , \qquad (1)$$

where $D_0^0(Cl_2)$ is the dissociation energy of the chlorine molecule [4], and ϵ_R is the energy (translational, rotational, vibrational) of the reactants. Using a value of 5136 Å for the shortest wavelength emitted by $BaCl^*$ and 6359 Å for that emitted by $SrCl^*$, we obtain from eq. (1) the values $D_0^0(BaCl) \geqslant 110$ kcal/mole and $D_0^0(SrCl) \geqslant 99$ kcal/mole, where ϵ_R has been estimated to have the value 0.1 eV. The dissociation energies we have calculated in this manner are slightly higher than the most recent mass spectrometric values obtained by Hildenbrand [5], who finds $D_0^0(BaCl) = 105.0$

± 3 kcal/mole and $D_0^0(SrCl) = 95.9 \pm 3$ kcal/mole.

From the variation of the chemiluminescent light intensity with Cl_2 pressure (shown in fig. 2a), it is possible to estimate the total reactive cross section σ for the collision process $Ba + Cl_2$ by fitting the light intensity to the formula

$$I = C [Cl_2] \exp \{-\sigma l [Cl_2]\} , \qquad (2)$$

where $[Cl_2]$ is the chlorine-molecule concentration, and l is the path length of the metal beam. For $Ba + Cl_2$, we calculate σ to be 60 $Å^2$. Note that an electron-jump mechanism [8] for the reaction $Ba + Cl_2 \rightarrow BaCl^\dagger + Cl$ predicts a value of $\sigma = 50 \ Å^2$, which is in remarkably good agreement with our estimated phenomenological cross section. Moreover, the weak intensity of the chemiluminescence suggests that the predominant product of the $Ba + Cl_2$ reaction does not radiate in the visible spectrum and is the BaCl molecule, vibrationally and rotationally highly excited but in the ground electronic state. Further evidence for the existence of highly excited ground-state BaCl molecules is provided by the presence of the Ba-emission line $6s6p$ $^1P^0 - 6s^2 \ ^1S$ (see fig. 1), which shows a first-order dependence on the Cl_2 pressure but a second-order dependence on the Ba pressure. This atomic resonance line is reminiscent of the diffusion-flame studies of Polyani [9] on the reaction $Na + Cl_2$. However, in the case of $Ba + Cl_2$, the precursor responsible for the atomic fluorescence is believed to be the vibrationally excited metal halide, rather than the metal-dimer molecule.

REFERENCES

[1] Ch. Ottinger and R. N. Zare. Chem. Phys. Letters 5 (1970) 243.

[2] G. Herzberg, Molecular spectra and molecular structure, Vol. 3 (Van Nostrand. Princeton. 1966) p. 454.473.

[3] K. H. Becker. W. Groth and D. Thran. Chem. Phys. Letters 6 (1970) 583.

[4] R. J. LeRoy and R. B. Bernstein. Chem. Phys. Letters 5 (1970) 42.

[5] D. L. Hildenbrand. J. Chem. Phys. 52 (1970) 5751.

[6] L. Wharton, R. A. Berg and W. Klemperer. J. Chem. Phys. 39 (1963) 2023.

[7] J. Gole, private communication; E. F. Hayes. J. Phys. Chem. 70 (1966) 3740.

[8] D. R. Herschbach. Advan. Chem. Phys. 10 (1966) 319.

[9] M. Polyani, Atomic reactions (Williams and Norgate. London. 1932).