

CROSSED BEAM CHEMILUMINESCENCE *

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Chemiluminescence spectra from reactions of Ba and Ca with NO_2 and N_2O were observed and 16 bands were assigned to the $\text{BaO A } ^1\Sigma - \text{X } ^1\Sigma$ system for $\text{Ba} + \text{NO}_2$. From this, a lower limit of 5.74 eV (133 kcal/mole) is placed on the BaO ground state dissociation energy. $\text{Ba} + \text{N}_2\text{O}$ shows large angle non-reactive scattering while $\text{Ba} + \text{NO}_2$ reacts at every collision (cross section $\gtrsim 150 \text{ \AA}^2$). An electron jump mechanism is proposed.

1. INTRODUCTION

Chemiluminescent reactions are usually observed in relatively high-pressure sources, such as flames and flowing afterglows, where secondary collisional processes often complicate the spectroscopic analysis. In the present work we have overcome this difficulty by employing crossed molecular beams for studying molecular emission. Thus molecular beam studies, already well-established with measurements of the angular and velocity distribution of products (for recent reviews, see refs. [1-4]), are extended into the regime of spectroscopy. This gives promise of providing detailed information about the disposal of excess energy in an exothermic reaction. We repeat here a first study of molecular chemiluminescence obtained by crossing atomic beams of various metals with different oxidizer gases†.

2. EXPERIMENTAL

Chips of Ba metal and Ca turnings were vaporized in a Mo crucible (0.8 cm in diameter and 3.6 cm deep). The crucible was heated to about 1100°C by radiation from a resistance-heated graphite cylinder which surrounded it. The atomic beam emanating from the crucible enters the reaction chamber from below and crosses a horizontal gas beam of N_2O or NO_2 which effuses through rather coarse crinkly-foil slits. Since no provisions were made for collimating the gas beam it consisted of a wide cone which filled most of the reaction chamber. The rather well-collimated atomic beam was about 8 cm in length from the crucible to the reaction region with a diameter of about 2 cm in the reaction region.

The pressure in the reaction chamber was varied between 2×10^{-5} and $> 1 \times 10^{-3}$ torr as measured by an ionization gauge. Even at the highest gas pressures, the pressure in the differentially pumped oven chamber was only on the order of 5×10^{-5} torr. This illustrates why the present work required at least one beam, although its directional properties were not exploited. It would have been impossible to operate the oven directly in the strongly oxidizing N_2O or NO_2 atmosphere.

Light from the reaction region was analyzed using a Heath 700 scanning monochromator ($f/7$, $34 \text{ \AA}/\text{mm}$, 50 to 200μ slits) to which an EMI 6256 photomultiplier (SQ) was attached. To monitor possible drifts or fluctuations in the beams, part of the overall light was diverted

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† Previously, upper limits for chemiluminescence of O_3 with NO , CO , H_2S and CS_2 were determined from cross-beam studies [5]. For cross-beamed studies of atomic chemiluminescence see ref. [6].

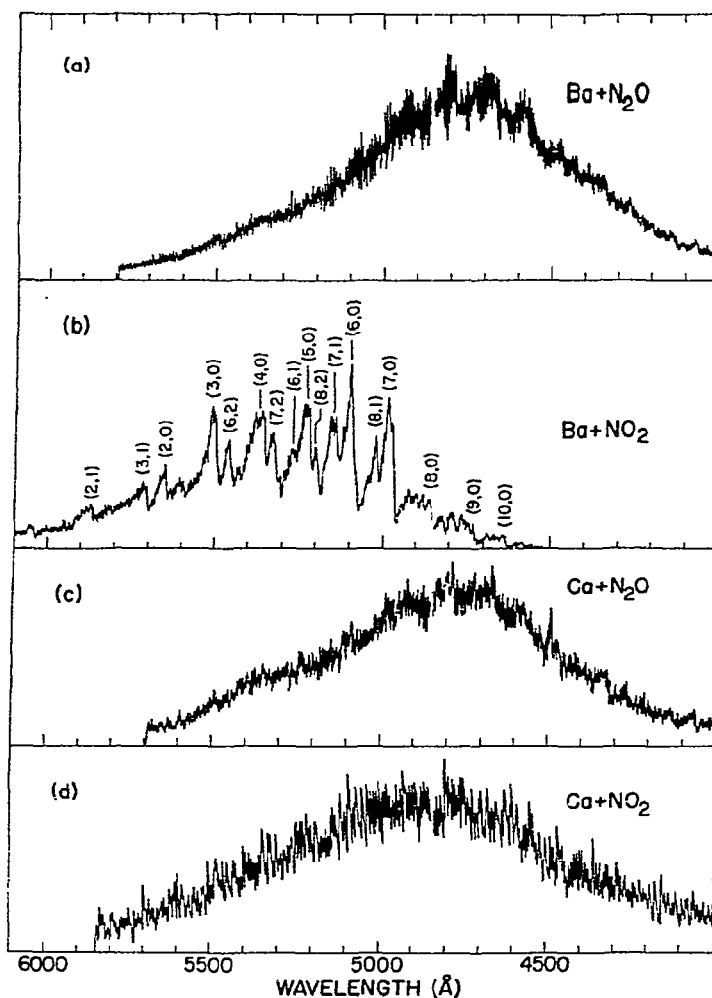


Fig. 1. Chemiluminescence spectra. The overall light intensity was monitored separately and was constant within $\pm 10\%$ during each scan. The $\text{Ba} + \text{NO}_2$ spectrum is severely suppressed at the long wavelength end by the fall off of the photomultiplier sensitivity.

before it entered the spectrometer and recorded simultaneously with the scan of the spectrum.

3. RESULTS AND DISCUSSION

Light from the Ba reactions was sufficiently bright to be easily seen with the room lights on. It appeared greenish-blue with N_2O and lemon yellow with NO_2 . The colors of the light from the Ca reactions were less distinct, but with the same trend. Chemiluminescence was also seen using metal beams of Mg, Na and Li with N_2O and NO_2 but the study of these systems was not

pursued. The fact that light can be observed indicates that these reactions possess no appreciable activation energy.

Fig. 1 shows the resulting chemiluminescence spectra uncorrected for wavelength response. Strikingly, only the Ba spectra are clearly structured, and of these only the $\text{Ba} + \text{NO}_2$ spectrum can easily be identified. The bands are labeled by comparing them with the band head wavelength of the $\text{BaO } A^1\Sigma - X^1\Sigma$ system [7,8]. The emitter is positively identified for just one of the four reactions. However, it is very likely that in at least three of the four reactions the emitting molecule is BaO or CaO, respectively. From the

metal consumption the flux in the reaction region is calculated to be approximately 10^{16} atoms/cm² sec. Since the metal beam intensity was not directly monitored, an accurate comparison between Ba and Ca is difficult. However, it seems that the light yield from the Ca reaction is at least one order of magnitude less than that of the Ba reactions.

The Ba + NO₂ spectrum (fig. 1b) permits a strict lower bound to be placed on the dissociation energy of the BaO molecule, a matter which has been the subject of much controversy [9]. The last clearly observed band, (10, 0), corresponds to a photon energy, $h\nu = 2.68$ eV. The thermal energy of relative motion of Ba and NO₂ is $E_{th} = 0.05$ eV and the dissociation energy $D(\text{NO-O}) = 3.115$ eV [10]. From the relationship, $D(\text{BaO}) - D(\text{NO-O}) + E_{th} \geq h\nu$, we find that $D(\text{BaO}) \geq 5.74$ eV (133 kcal/mole). The actual value of $D(\text{BaO})$ may be somewhat higher than this limit since (1) the NO reaction product may carry off vibrational, rotational and translational energy, and (2) the rapid fall off with ν' of the Franck-Condon factors $q_{\nu'\nu''}$ suggests that the (10, 0) wavelength cutoff may not represent the highest vibrational level populated by the Ba + NO₂ reaction. Previous literature values for the BaO dissociation energy show considerable scatter with 108.4 kcal/mole by Herzberg [11], 117.6 kcal/mole by Kalff et al. [12], 125.9 ± 2 kcal/mole by Schofield [13], 127.5 ± 7 kcal/mole by Brewer [14], 133 ± 3 kcal/mole by Gaydon [15] and 145 kcal/mole by Mahanti [16]. The lower limit we have deduced for $D(\text{BaO})$ rules out some of the prior determinations.

The Ba + NO₂ spectrum allows, in principle, a direct determination of the relative initial population $N(\nu')$ of the upper state vibrational levels. The relative intensity of most of the bands can roughly be estimated from the peak heights of the bands shown in fig. 1b, where corrections are made for spectral response of the detector (measured with a calibrated tungsten lamp) and fluctuations in the beam flux. The $N(\nu')$ distribution (table 1) is then obtained from the corrected peak heights by dividing them by $q_{\nu'\nu''}\nu^4$, where $q_{\nu'\nu''}$ is the Franck-Condon factor* and ν the frequency of the (ν', ν'') band head. No corrections were made for the unresolved rotational structure and the possibility of blended features. This as well as the possibility of other electronic states may contribute to the large inconsistencies in the values of $N(\nu')$ apparent in the comparison of the rows of table 1.

* Calculated using the programs documented in ref. [17].

Table 1
Relative intensities of the identified bands from Ba + NO₂ chemiluminescence. The intensities are normalized to 1.00 for the (6, 0) band

| $\nu'' \backslash \nu'$ | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-------------------------|------|------|------|------|------|------|------|------|------|
| 0 | 1.07 | 1.34 | 0.50 | 0.48 | 1.00 | 0.80 | 2.73 | 2.18 | 2.48 |
| 1 | 0.87 | 1.37 | | | 0.64 | 0.62 | 0.36 | | |
| 2 | | | | | 1.50 | 4.3 | (a) | | |

(a) The feature marked (8, 2) in fig. 1 at 5200 Å has an anomalous intensity and is suggested by Sakurai et al. [25] to belong to another band system.

Inspection of fig. 1b and table 1 shows that the Ba + NO₂ reaction is not specific to one or two ν' levels but may preferentially populate $\nu' = 8, 9$ and 10. Previously, information on the $N(\nu')$ distribution of a chemical reaction has been obtained from infrared emission studies [18]. The present approach is complementary. Although limited to highly exothermic reactions, it has the advantage that collisional degradation of the initial $N(\nu')$ can be neglected at much higher pressures than in the infrared work, since the radiative lifetime of the electronically excited states is much shorter than that of the infrared emitting reaction products.

To determine the reaction order of the chemiluminescent process illustrated in fig. 1, the light yield at a fixed wavelength (5200 Å) was measured as a function of gas pressure. The functional dependence is presented in fig. 2. All reactions except Ca + NO₂ show a linear initial rise indicative of a simple bimolecular mechanism. For Ca + NO₂ the onset is clearly quadratic in the NO₂ pressure. To test whether the light production depends on a three-body collision process, air was admitted while the NO₂ pressure was held constant. No change in the light intensity was observed. The quadratic pressure dependence for Ca + NO₂ may have more than one interpretation. One possibility is that the light is produced by the reaction $\text{Ca} + \text{N}_2\text{O}_4$, where the N₂O₄ present is proportional to the square of the NO₂ pressure. This seems somewhat surprising since (1) N₂O₄ might be expected to behave chemically much the same as NO₂ and (2) little N₂O₄ is present at the low NO₂ pressure used. Perhaps a more likely possibility is that the Ca + NO₂ reaction produces highly vibrationally excited ground state CaO molecules which, in turn, react with themselves or with NO₂, to produce chemiluminescence from a polyatomic metal oxide emitter. Fig. 2 shows that the reac-

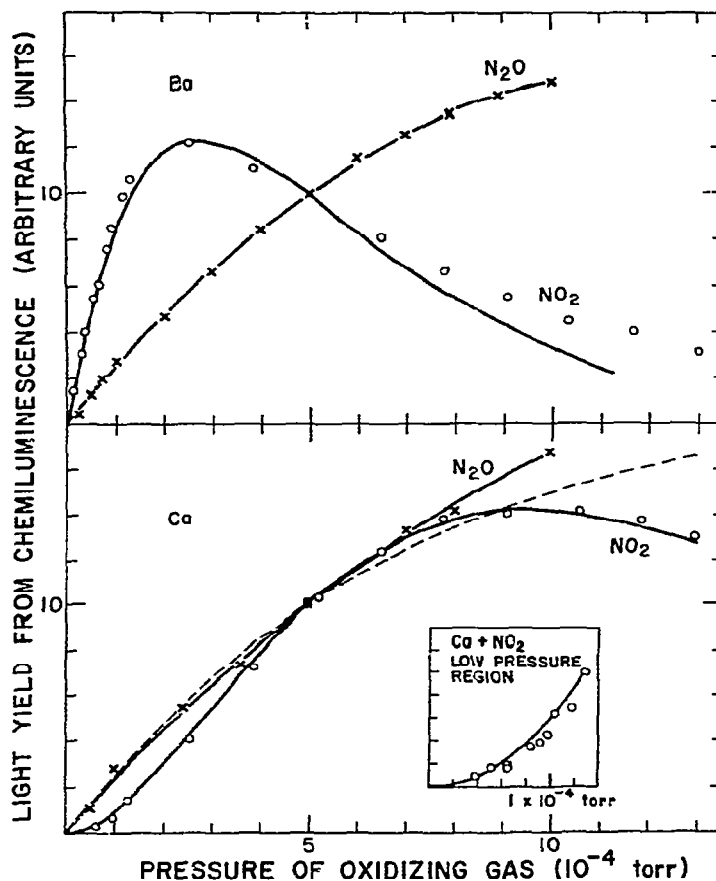


Fig. 2. Dependence of chemiluminescence intensity at 5200 Å on reactant gas pressure. The intensities are normalized to 10 at 5×10^{-4} torr. The solid curves are calculated fits based on $p e^{-\alpha p}$ ($p^2 e^{-\alpha p}$ for $\text{Ca} + \text{NO}_2$). The dashed curve of $p e^{-\alpha p}$ for $\text{Ca} + \text{NO}_2$ demonstrates that this law cannot fit the $\text{Ca} + \text{NO}_2$ data.

tion $\text{Ba} + \text{NO}_2$ may also have a small quadratic contribution to its pressure dependence.

At higher pressures all plots reflect the attenuation of the metal beam between the entrance to the reaction chamber and the crossed beam intersection region. This attenuation is seen to be of very different degree, i.e., much stronger for the NO_2 than for the N_2O reactions.

For the $\text{Ba} + \text{NO}_2$ reaction the strong attenuation can most dramatically be seen by directly viewing the chemiluminescence. Especially instructive is a comparison with $\text{Ba} + \text{N}_2\text{O}$. At low pressures ($\sim 5 \times 10^{-5}$ torr) a rather slender, well defined Ba beam can be observed emerging from the entrance hole. As the gas pressure is increased, the beam becomes more intense, but also changes shape. For N_2O , the beam begins to fan out, becomes mushroom-shaped and finally forms an approximately hemispherical cloud

above the entrance hole. For NO_2 , the behavior is totally different. The beam simply becomes shorter and shorter with increasing pressure, until at extremely high pressure it is "pushed back" into the entrance hole, never showing any signs of fringing or spreading.

Obviously with N_2O a considerable fraction of the Ba atoms is scattered at large angles ($\geq 30^\circ$) without reaction and then reacts outside the original beam. With NO_2 this does not occur, but rather we have "reactions at every collision", a phrase first introduced by M. Polanyi [19] to describe the alkali-atom-halogen-molecule ($\text{M} + \text{X}_2$) reactions.

The curves in fig. 2 were fit to the experimental points assuming that they obeyed a $p e^{-\alpha p}$ relationship ($p^2 e^{-\alpha p}$ for $\text{Ca} + \text{NO}_2$). Here the term linear (quadratic) in p describes the formation of excited-state molecules and the exponential term $e^{-\alpha p}$

Table 2

Pressure dependence parameters of chemiluminescence measured at 5200 Å

| Reaction | Assumed law | α (torr ⁻¹) | σ (Å ²) |
|-----------------------|---------------------|--------------------------------|----------------------------|
| Ba + N ₂ O | $p e^{-\alpha p}$ | 600 | 36 |
| Ba + NO ₂ | $p e^{-\alpha p}$ | 3600 | 220 |
| Ca + N ₂ O | $p e^{-\alpha p}$ | 360 | 22 |
| Ca + NO ₂ | $p^2 e^{-\alpha p}$ | 2080 | 125 |

describes the attenuation of the metal beam by the oxidizer gas. The attenuation parameters α are listed in table 2 along with their corresponding attenuation cross section (based on a beam path length of 4.5 cm).

The pressure was measured by an ionization gauge above the pump some distance away from the reaction region, where the pressure may have been lower by 50%. The NO₂ pressure was related to the N₂O pressure using a thermocouple gauge which responds equally to NO₂ and N₂O because of their similar molecular weight. The N₂O pressure was assumed to be given directly by the ion gauge reading. The cross sections in table 2 are phenomenological cross sections, comprising all attenuation effects. The values of α were calculated neglecting the possible pressure differential between reaction region and ion gauge and may be systematically high by ~ 50%. The contribution to these cross sections from small angle scattering can be ignored since short, thick beams were used. For Ba + NO₂, where large angle scattering has been shown in this study to be insignificant, the cross section in table 2 represents the total reactive cross section; for N₂O it represents only an upper bound.

In addition to chemiluminescence, the total reactive cross section includes production of ground state metal oxide molecules. In fact it can be concluded that the large reactive cross section for Ba + NO₂ is *mostly* caused by the reaction yielding ground state BaO. At 5×10^{-5} torr (where there is little beam attenuation) the total light yield from the Ba + NO₂ reaction is found to be 1.75 ± 0.3 times *smaller* than the Ba + N₂O reaction in spite of the fact that the total reactive cross section for Ba + NO₂ is about 6 times *larger* than Ba + N₂O (the more exothermic reaction). For the Ca reaction, too, the N₂O cross section is much smaller than the NO₂ cross section. Compared with Ba, the Ca cross sections for both reactions are much reduced. Qualitatively, the spreading of the Ca + NO₂ chemiluminescence with increasing pressure seemed to be intermediate between Ba + NO₂ and Ba + N₂O.

The magnitude of the reactive cross section for Ba + NO₂ is reminiscent of the alkali-atom-halogen-molecule reactions (prototype: K + Br₂). It suggests that here, too, an electron jump mechanism is operative [1]. Although Ba (I.P. = 5.21 eV) is not as readily ionized as K (I.P. = 4.339 eV), the vertical electron affinity of NO₂ ($E_a = 3.15 \pm 0.05$ eV [20,21]^{*}) exceeds that of Br₂ ($E_a = 2.16 \pm 0.1$ eV [22]). The electron jumping radius r_c can be estimated from $e^2/r_c = \text{I.P. (Ba)} - E_a(\text{NO}_2)$, and the total reactive cross section $\sigma_{\text{Ba}+\text{NO}_2}$ is greater than [23], or equal to, πr_c^2 , i.e. $\sigma_{\text{Ba}+\text{NO}_2} \geq 150 \text{ Å}^2$.

The vertical electron affinity of N₂O is unknown but is expected to be quite small, if not negative, because of the change in geometry between the N₂O and N₂O⁻ equilibrium configurations [24]. This suggests a reason why Ba + N₂O collisions, even at relatively small impact parameters, lead to large angle scattering rather than to reaction. Similarly, for the Ca + NO₂ system, Ca with its higher ionization potential (6.111 eV) might be expected to have a two-thirds smaller electron jumping radius and hence a four-ninths smaller total reactive cross section, in rough agreement with the experimental findings presented in table 2.

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* O. E. Wagner reported a value for the NO₂ electron affinity of 2.6 ± 0.15 eV obtained by a quite different technique.

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