Chemiluminescence from mixtures of Ba+CO₂ and Ba+CO

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Broad banded chemiluminescence has been detected from the reaction of Ba+CO₂ and Ba+CO in a heat pipe. Extending from 500 to 1150 nm, the spectrum of this flame exhibits several prominent peaks. The emitting species has not been identified; however, evidence favors a polyatomic molecule. The observation of such chemiluminescence from apparently endoergic reactions is of interest and importance for the understanding of chemiluminescent processes.

A bright red–orange flame has been observed from the reaction of Ba+CO_2. This same spectrum, but weaker in intensity, has also been detected from the reaction of Ba+CO. The reactions take place in a heat pipe reactor at pressures of approximately 100 Pa and temperatures around 1125 K. Observed flame spectra extend from 500 to 1150 nm and have continuumlike appearance with several broad features. One of the most prominent spectral features occurs near 850 nm and in the following discussion, the term "850 nm system" will refer to the entire observed emission system.

The appearance of the flame spectrum does not allow the emitting species to be identified, but irregularities in the spectrum suggest the candidates should include polyatomic as well as diatomic species. A diatomic reaction product of Ba+CO_2, ground state BaO, is observed in the heat pipe, but the emission is not from any of the identified systems of this molecule. However, the broadness and lack of identifiable progressions in the spectrum suggests the emitter could be polyatomic and one such candidate is BaCO. Since in previous studies of metal atom chemiluminescent reactions the identified emitters have always been diatomic or atomic species, the possibility for investigation of an interesting set of reaction dynamics exists if the emission is indeed due to a polyatomic molecule.

EXPERIMENTAL

Emission from the reaction of Ba with CO_2 is observed in a crossed, stainless steel heat pipe. Details of the apparatus are reported elsewhere.[1] Therefore, only a brief description is given here. The heat pipe consists of two 5 cm diameter, 65 cm lengths of stainless steel pipe joined to form a cross. Barium metal is placed in the lower vertical arm, which is heated by an rf induction heater. The remaining three arms are heated by resistance heaters, and the temperature is monitored by chromel–alumel thermocouples spot welded to the exterior wall of the heat pipe. High purity helium (99.995%) is used as a buffer gas at the cool zones of the heat pipe, and the buffer gas pressure is monitored by a capacitance manometer.

Spectra of flames are obtained with a $\frac{3}{4}$ m Fastie-Ebert monochromator which observes the reaction region through a quartz window located at the end of one of the horizontal arms of the heat pipe. This instrument is equipped with 500 μm slits, a 600 line/mm grating blazed at 1000 nm, and a cooled, S-1 surface photomultiplier tube. The resulting resolution element of the monochromator is about 1.5 nm. An argon ion laser can be used to excite photoluminescence in nonemitting reaction products. In these experiments, the laser beam enters through a window at the top of the vertical arm. Photoluminescence is then observed at right angles to the laser by the monochromator.

To observe the reaction, CO_2 (99.5%) or CO (99.999%) is admitted to the central metal vapor zone of the heat pipe through a 3 mm diameter stainless steel tube. In typical experimental conditions, the CO_2 flow rate is about 3.5×10^{19} molecules/sec. Required CO reactant flow rates are slightly higher. During operation the total pressure in the system remains constant and it is assumed that the reaction end products either condense as solids or are gettered by the barium.

The flame resulting from the Ba+CO_2 reaction is red–orange in color and is spherically diffuse at these pressures. It is uniformly intense for a sphere of about 40 mm in diameter and is confined below the CO_2 inlet pipe. Figure 1 shows the spectrum of this flame from 580 to 1125 nm. The lower spectrum shows the raw data, uncorrected for the detection system response, with the dashed trace indicating the spectral contribution of black body radiation from the heat pipe walls. In the upper spectrum, this black body contribution has been subtracted and the spectrum corrected for instrument response. Table I lists the wavelengths of the prominent features.

No relative changes in intensity of the various spectral features are observed over the pressure range 30–150 Pa, but the overall emission intensity does decrease at pressures above about 120 Pa. When CO is substituted for CO_2 the same spectrum is observed with about two orders of magnitude decrease in intensity. To check that the CO flame was not due to a CO_2 impurity, the CO was cooled to 178 °K with no change in emission. Cooling to 77 °K produced reduced intensity due to the decreased CO vapor pressure. When CO_2 was cooled to 178 °K the flame disappeared entirely.
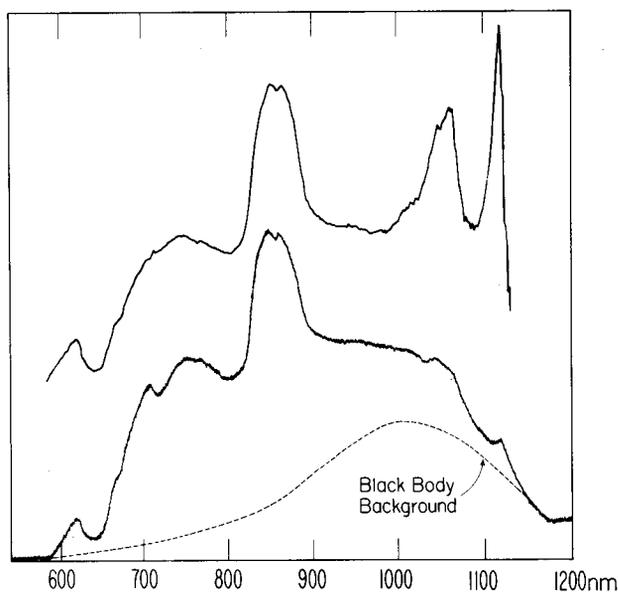
FIG. 1. Spectrum of the flame provided by the Ba+CO₂ reaction with total pressure of 65 Pa and temperature of 1125°K. The lower trace is uncorrected for instrument response function and includes heat pipe blackbody emission (indicated by dashed line). Represented in the upper trace is the spectrum corrected for both the black body and instrument response effects. This spectrum was obtained using a $\frac{3}{4}$ m Fastie–Ebert monochromator equipped with a cooled, S-1 response photomultiplier and a 600 line/mm grating blazed at 1000 nm (resulting in a resolution element of 1.5 nm).

DISCUSSION

The detection of broad banded emission from the flames of BA +CO as well as Ba +CO₂ raises the possibility of polyatomic chemiluminescence or luminescence from a perturbed excited state of a diatomic. However, experimental conditions are not suitable to differentiate between possible emitters and no simple reaction scheme is sufficiently exoergic to produce the chemiluminescence, making assignment of this system to a specific emitter very difficult.

No well defined bandheads or progressions have been found in the flame spectrum to aid emitter species identification. Toward the blue is a weak band at 520 nm, which appears structureless at our resolution. The prominent band system, starting at approximately 600 nm and continuing into the infrared, consists of broad bands with intensity maxima, but containing no sharp, bandheadlike features. No progressions are evident over the entire spectral region, which is nearly 600 nm wide. This lack of spectral regularity suggests the emitter is either a highly perturbed electronic state of a diatomic or some polyatomic species, but spectral evidence is not complete enough to distinguish between the possibilities.

Comparison of the 850 nm system to the well-known BaO visible chemiluminescence[1–3] from the Ba +N₂O reaction is useful for elucidating some characteristics of the emitting species or its kinetics. The 850 nm band appears orders of magnitude less intense, but still easily visible to the unaided eye. Also, the 850 nm sys-

tem nearly fills the heat pipe volume with uniform intensity, while the flame from the Ba +N₂O system under similar conditions is extremely intense close to the N₂O inlet nozzle with decreasing intensity filling the rest of the volume. The small volume of extremely high emission intensity is consistent with both the rapid reaction kinetics of Ba +N₂O and the short lifetime of the $A\,^1\Sigma^+$ state of BaO. In a similar manner, two causes for the uniform luminescence of the 850 nm system can be postulated. Either (1) the emitting state has a long lifetime and can travel through relatively long distances before emitting and/or (2) the kinetics leading the formation of this species are slow or multistep. These experiments do not differentiate between these two mechanisms. The reduced intensity of the 850 nm system relative to the allowed transition in BaO produced by the energetically favorable reaction of Ba +N₂O is also consistent with mechanisms suggested above. Other factors discussed below also imply that at least one of three mechanisms, multistep kinetics, is probably occurring.

Similar relative intensities for the entire flame spectrum were obtained under all experimental conditions, suggesting a single mechanism is operative for both CO₂ and CO for the pressure range of 30 to 150 Pa. Species with lifetimes as short as the BaO(A) state show some collisional relaxation at even our lowest pressures[2]; it is therefore possible that the 850 nm system is from a completely relaxed state rather than a totally unthermalized state over the entire pressure range. This inferred Boltzmann distribution in the lowest levels of the emitter electronic state can be the result of a state that is long lived, has an exceptionally large collision cross section, or is initially prepared in the lowest vibrational levels. Whatever mechanism is responsible for emission, there is probably only a single channel for this decay over our entire pressure range and for both CO and CO₂ since it is highly improbable that more than one mechanism would give the same results for all conditions.

Neither the Ba +CO₂ or Ba +CO systems have obvious sources of energy sufficient to form an excited molecule at least 1 eV above the ground state. The heat pipe environment with a temperature of approximately 1125 °K gives an average kinetic energy about 10 times less than that of the emitted radiation. Excited reactant states are also minimally populated with less than 10^{-5} of the Ba in the ^1D, ^3D (lowest excited) states at

TABLE I. Listing of prominent features in the Ba+CO₂ reaction flame.

λ (nm)	E (cm⁻¹)	E (eV)
522	19 160	2.38
622	16 080	1.99
760	13 160	1.63
850	11 770	1.46
864	11 580	1.44
1050	9 530	1.18
1128	8 870	1.10

1125 °K. Although CO and CO$_2$ have significant popula-
tions of vibrationally excited ground state molecules,
virtually none are in excited electronic states. To fur-
ther demonstrate that energy need not be added to the
reactants, the same flame has been observed at lower
temperatures in a Ba rich flow system.[4] Thus, no
great amount of energy need be supplied to the reactants
from the experimental environment.

There are no obvious reaction mechanisms for which
enough excess energy is supplied by the ground state
reactants. The reaction Ba +CO$_2$ → BaO +CO is exoergic
by only about 0.3 eV. Evidence that this reaction oc-
curs in the heat pipe is the detection of ground state,
but not excited state, BaO. Ground state BaO is de-
tected by photoluminescence after excitation by the 488
nm line of an Ar$^+$ laser. No emission from the BaO (A)
state is observed in the absence of laser excitation.
No simple reactions of the ground states of Ba +CO are
expected to be exoergic. However, it should be noted
here that Ba +O$_2$ does not contain enough energy to ex-
cite BaO (A) by the reaction Ba +O$_2$ → BaO +O, but chemi-
luminescence is seen in that system.[5,6] For all these
systems multistep reaction schemes appear necessary
to obtain excited species.

Some possible emitter candidates will be discussed
with respect to energetic and kinetic considerations
mentioned above:

BaO excited state. Luminescence from the A state
is not seen in these experiments, so that if BaO is the
emitting molecule the state must lie below the A state.
Recent calculations place all other low lying states in
BaO slightly above the A state.[7] Also, it is difficult to
find a mechanism to produce excited BaO from Ba +CO
because of the approximately 11 eV bond energy of CO.

BaC. This is energetically more diffiult to produce
than BaO.

Ba$_2$. Since the 850 nm system has been observed

under Ba rich conditions[4] in a flow system of Ba +CO$_2$,
the emission might be due to Ba$_2$. Only ground state Ba
is present in the initial system, making it difficult to
produce excited state Ba$_2$ by a simple mechanism. This
spectrum is not seen in Ba rich systems without CO or
CO$_2$ present and it is implausible that both CO and CO$_2$
and only these two molecules would be active in produc-
ing a Ba$_2^*$ species.

BaCO. The same energetic arguments used above
apply here. The ground states of Ba and CO are not
favorable either energetically or configurationally to
form BaCO. Because of the high energy of excited CO
states it is unlikely that CO* could be involved in BaCO*
formation. Ba*+CO might not result in bound states.
Certainly a multistep reaction scheme would be neces-
sary to form this molecule in an emitting excited state.

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