CHARACTERIZATION OF THE CHEMILUMINESCENCE OBSERVED DURING THE REACTION BETWEEN LEAD VAPOR AND $^{3}\Sigma$ O₂

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The chemiluminescence observed during the reaction between lead vapor and ground state oxygen $\binom{3}{2} \Sigma O_2$) was analyzed. The spectral bands could be assigned to transitions from the a, A, B and C electronic states to the ground state. Evidence is presented to indicate that the reactive lead vapor is generated thermally rather than electrically.

1. Introduction

Recent attempts to spectrally resolve the chemiluminescence which occurred during the reaction between lead vapor and ground state oxygen $(^{3}\Sigma O_{2})$ have been unsuccessful. This lack of success occurred either because the intensity of the emission was too weak [1] or because such severe clogging of the lead crucible opening occurred as to prevent a full characterization of the chemiluminescence [2] during the time available.

In the present work, lead vapor was reacted with ${}^{3}\Sigma O_{2}$ in a flow tube reactor and chemiluminescence was observed. The emission was analyzed spectroscopically and emission from several bands was observed and identified. Emission was observed from the a, A, B and C states to the ground state of lead oxide (PbO).

2. Experimental

The experimental apparatus to generate chemiluminescent PbO flames and to analyze the chemiluminescence was a flow tube reactor system. A schematic diagram of the flow tube reactor is shown in fig. 1.

The flow tube was constructed of 3" inner diameter stainless steel (Alloy Products Corp. 2, Waukesha, WI). Sections of the tube are connected by means of quick flange connectors fastened with heavy duty clamps. Vacuum tightness (to 0.05 mm) is ensured at the flanges



Fig. 1. Flow tube reactor system.

by Viton O-ring seals. A cross in the flow tube above the furnace section formed the burner section in which the chemiluminescent flame was formed and could be observed. A 4" extension was used on the arm facing the monochromator. A quartz flat was placed on the end of this extension to serve as the observation window The manner in which the flow tube is configured is critical with respect to forming deposits on the observation window. It has been found that the configuration adopted in the present study resulted in negligible deposition on this window.

A glass wool particle trap prevented ingestion of solid reaction products by the vacuum system. Dynamic pressures in the flow tube were measured downstream of the particle trap with an MKS Baratron 77 pressure meter.

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Fig. 2. Furnace chamber used to vaporize lead.

The furnace and chimney assembly is located immediately below the burner region. It is attached to the lower part of the flow tube cross. A schematic representation of the furnace chamber is shown in fig. 2.

Granular lead was resistively heated in a 1" diameter by 1" alumina crucible (R.D. Mathis Co.). A tungsten wire basket heater (R.D. Mathis Co.) held the crucible. The heater wire was insulated on one side with zirconia cloth (Zircar Products) to improve heating efficiency. The heater leads were attached to brass electrodes which were electrically insulated from the flow tube by teflon swagelock fittings (Nacon Industries). These teflon fittings consist of three pieces that, when secured, give a vacuum tight seal. Water flowing through $\frac{1}{8}$ " copper coils, wrapped around the electrode supports, cooled the electrodes.

Argon gas was introduced into the furnace chamber to entrain lead vapor and transport it to the reaction area via the chimney. The chimney was made of a thin walled 0.5" outer diameter stainless steel tube. A precisely machined glass ceramic transition section linked the crucible to the chimney. The glass ceramic was manufactured by the Corning Glass Works. It is sold under the trade name MACOR. This ceramic is machineable and useful up to temperatures of 1200°C.

The glass ceramic was machined to loosely fit between the chimney and crucible. The loose fit was to prevent thermally induced stresses from occurring between the different materials at operating temperatures. Four tangential holes, $\frac{1}{16}$ diameter, were drilled into the ceramic about $\frac{1}{8}$ from the bottom to allow carrier gas to enter the crucible and mix with the lead vapor.

The chimney was held in place by a 0.5" inner diameter Cajon connector (replacing the conventional Oring with an aluminum one). This arrangement allowed easy replacement of badly lead-coated chimneys and adjustment of chimney position.

When the mixture of carrier gas and lead vapor reached the reaction area, it was mixed with oxidizer to produce a flame. The oxidizer manifold consisted of a short annular piece approximately 1" long by $l\frac{1}{2}$ " outer diameter, fabricated of stainless steel. The manifold was placed at the top of the lead vapor chimney and formed an extension of it. A series of holes were drilled into the upper half of the inside surface. The holes were spaced 90° apart radially and $\frac{1}{4}$ " apart vertically in alternating rows. They were drilled with a #70 drill bit at an angle of 25° below the horizontal so as to direct the oxidizer to the center of the chimney region. The holes were extended to the top of the manifold where a row was spaced 45° apart radially and a final series of holes spaced 22.5° apart radially were drilled at the top of the manifold in order to direct oxidizer at an angle of 45° into the flame region, thus to provide a gas curtain to contain the flame.

A 3" diameter planar—convex lens of 25 cm focal length was used to collect the light from the flame. A 3" diameter planar—convex lens of 50 cm focal length was used to focus the light onto the entrance slit of a Jarrell-Ash 0.5 m Ebert mount monochromator with a grating (1180 groove/mm blazed at 5000 Å). A slit width of 150 μ m was used for maximum signal strength. The optical train was aligned with a HeNe Laser. An RCA C31034-02 PMT, operated at -20° and biased with a Keithley 244 high-voltage power supply, was used as a detector. The signal was amplified and fed into a strip chart recorder. Spectra were calibrated with mercury, neon, krypton, xenon and argon Oriel pen lamp calibration sources. Resolution of spectral lines with the experimental arrangement was determined to be 5 Å fwhm.

An iron-constantan thermocouple placed directly above the crucible measured vapor temperatures of $760-890^{\circ}$ C. The temperatures in the flame region, as determined by a chromel-alumel thermocouple, were $175-190^{\circ}$ C.

Mass deposition experiments were carried out at

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890°C to determine the number density of lead present in the reaction area during the normal flow tube operation. The mass balance achieved was 98%. It was found that 36% of the lead actually made it to the reaction area. A measurement of the deposition pattern in the reaction area showed that very little lead left the area above the chimney (the flame region). This means that the vapor flow velocity is fairly fast, leaving little time for the lead vapor to diffuse and so lead flow is well collimated. The flux of lead atoms was calculated to be 2.8×10^{18} atoms/cm² s. The mass flow rate was determined at 2 Torr total pressure with a mass flow meter (Hastings model No. H-10K) and the gas velocity was calculated to be 8150 cm/s of lead atoms and the number density of lead atoms was calculated to be 3.435×10^{14} atoms/cm³.

Two methods were used in an attempt to detect electrical excitation of Pb in the current work. First, one of the electrodes to the tungsten coil was grounded to the outside of the flow tube to prevent arcing across the electrodes. The emission intensities were recorded with and without the ground wire connected. No observable change occurred in the intensities.

The second method used was to shut off the heater power supply and observe the resulting decay in emission intensity as a function of time and temperature. If electrical excitations were occurring, a sudden drop in intensity should have been observed. If no electrical excitations were occurring, the intensity decay should be gradual with time. Fig. 3 shows a plot of intensity and temperature versus time. Note the linearity of the temperature plot and the gradual decay of the intensity.

The intensities of emissions at selected wavelengths were observed under different pressure conditions.



Fig. 3. Emission intensity and temperature decay versus time for Pb + $O_2(^{3}\Sigma)$ reaction.

Table 1					
Activation	energies for	the	formation	of	PbO*

Wavelength observed (nm)	O ₂ pres- sure (Torr)	Ar pres- sure (Torr)	Pb vapor temperature (K)	Activation energy (Ea) (kcal/mol)	
670, 590.8	0.3	1.9	1044–1086	63.9 ± 8.0	
590.8,431.3	0.8	3.3	1062–1103	115.3 ± 22.4	

The intensities were observed as a function of lead vapor temperatures. From these observations a rough estimate of the activation energies (Ea) for the formation of excited lead oxide (PbO^*) were obtained [3]. The results of these experiments are presented in table 1.

3. Results and discussion

The chemiluminescence of PbO was observed during the reaction between Pb and ${}^{3}\Sigma O_{2}$. The emissions were sufficiently intense so that the spectral lines could be resolved. Spectra were observed over the range 400--800 nm. The vibrational band structure was evident in the spectrum. The rotational structure, shaded toward the red, could not be resolved; however, band head assignments could be made with a good degree of certainty in many cases. The spectrum obtained during the reaction between Pb and ${}^{3}\Sigma O_{2}$ is shown in fig. 4. The band head assignments are shown in table 2. Initial as-



Fig. 4. Chemiluminescence spectrum from the Pb + ${}^{3}\Sigma O_{2}$ reaction.

Table 2

Observed PbO bandheads and their assignments for the Pb + $O_2(^3\Sigma)$ reaction. All transitions are to the ground electronic state

Observed (Å)	Corrected (cm ⁻¹)	Calculated (cm ⁻¹)	Corr calc. (cm ⁻¹)	Assign- ment	Observed (Å)	Corrected (cm ⁻¹)	Calculated (cm ⁻¹)	Corr.— calc. (cm ⁻¹)	Assign- ment
5104.7	19584.4	19583.3	-1.1	a(8.0)	5070.2	19717.6	19736.9	19.3	A(0.0)
5219.3	19154.2	19146.3	-7.9	a(7.0)	5134.2	19471.9	19470.0	1.9	A(1,1)
5345.4	18702.4	18703.2	0.8	a(6.0)	5252.3	19033.8	19021.6	-12.2	A(0.1)
5475.8	18257.2	18253.8	-3.4	a(5.0)	5327.6	18764.9	18761.7	-3.2	A(1.2)
5590.3	17883.0	17889.2	6.2	a(9.3)	5402.4	18505.1	18504.4	-0.7	A(2,3)
5615.9	17801.5	17798.3	-3.2	a(4,0)	5464.4	18295.2	18313.3	18.1	A(0.2)
5699.9	17539.2	17538.5	0.7	a(5,1)	5537.1	18055.1	18060.3	5.2	A(1.3)
5767.2	17334.6	17336.6	2.0	a(3,0)	5671.8	17626.1	17611.9	-14.2	A(0.3)
5851.8	17084.1	17083.0	-1.1	a(4,1)	5758.2	17361.7	17366.0	4.3	A(1.4)
5927.0	16867.4	16868.7	1.3	a(2,0)	5905.3	16929.4	16917.6	-11.8	A(0,4)
6014.9	16620.7	16621.3	0.6	a(3.1)	5993.8	16679.2	16678.6	-0.6	A(1.5)
6099.1	16391.3	16394.7	3.4	a(1.0)	6155.0	16242.5	16230.2	-12.3	A(0.5)
6190.5	16149.3	16153.4	4.1	a(2,1)	6250.4	15994.6	15998.1	3.5	A(1.6)
6283.8	15909.6	15913.0	3.4	a(3.2)	6428.3	15551.9	15549.7	-2.2	A(0.6)
6377.9	15674.7	15679.4	4.7	a(1.1)	6522.7	15326.8	15324.7	-2.1	A(1.7)
6476.2	15436.9	15445.1	1.1	a(2,2)	6817.7	14663.6	14658.2	-5.4	A(1.8)
6579.0	15159.7	15199.2	3.5	a(0.1)	4063.5	24602.7	24605.4	2.7	B(5.0)
6677.9	14970.7	14971:1	0.4	a(1,2)	4143.0	24126.6	24130.4	3.8	B(4.0)
6782.7	14739.3	14743.8	4.5	a(2,3)	4223.8	23668.6	23651.6	-17.0	B(3.0)
6899.2	14490.4	14490.8	0.4	a(0.2)	4313.4	23177.1	23169.1	-8.0	B(2.0)
7002.5	14276.7	14269.7	-3.0	a(1,3)	4405.5	22692.7	22682.8	-9.9	B(1.0)
7245.7	13797.5	13784.5	-8.0	a(0.3)	4505.3	22189.7	22192.8	3.1	B(0.0)
7362.0	13579.6	13575.4	-4.2	a(1.4)	4551.6	21964.0	21967.6	3.6	B(1.1)
7632.1	13098.9	13095.1	-3.8	a(0.4)	4653.7	21482.3	21477.5	-4.8	B(0.1)
4446.5	22483.5	22487.7	4.2	A(8.1)	4704.3	21251.3	21259.2	7.9	B(1.2)
4645.7	21519.3	21504.6	-14.7	A(4,0)	4809.9	20784.8	20769.2	15.6	B(0.2)
4749.8	21047.8	21069.1	3.6	A(3,0)	4984.4	20057.0	20067.8	10.9	B(0,3)
4773.8	20942.0	20938.8	-3.1	A(6,2)	5158.2	19381.3	19373.5	-4.1	B(0,4)
4846.3	20628.3	20624.4	1.1	A(2.0)	5271.3	18965.3	18982.0	9.2	B(2,6)
4957.0	20176.8	20185.3	17.5	A(1,0)	5410.5	18477.5	18495.7	18.2	B(1.6)
5022.1	19906.4	19914.1	7.7	A(2,1)					- /- /

signments were made with the aid of Deslandres tables calculated from molecular constants reported in the literature [3,4]. A computer program called SEARCH [5] was used to find close matches between the observed wavelengths and calculated values in the Delandres tables. Where no ambiguities existed, the bandhead assignments were made directly from the computer printout. When two or more wavelengths fell close to the same calculated value, additional information was used.

Pow [6] was able to calculate a complete set of Franck-Condon factors for the a-X, b-X, A-X, B-X, C-X, C'-X, D-X and E-X transitions of PbO. These factors were used extensively to discern proper assignments based on the relative intensity of the bands. Assignments were made in such a way as to continue a progression unless the Franck-Condon factors were unfavorable for a particular transition. In addition, assignments reported in the literature were used in making the determinations. Analysis of the spectrum yielded 63 bands assignable to transitions from the a, A, B and C electronic states. In table 2 the bandhead positions reported in Å were the observed positions. The bandhead positions reported in cm⁻¹ were corrected for vacuum. Bandhead positions were also calculated by least-squares analysis of the data. The standard deviation between corrected and calculated bandhead positions was 7.9 cm⁻¹.

The experiments establish that only thermal excita-

tion is important in the lead vapor. The observation of chemiluminescence from electronically excited lead oxide (PbO^*), then is significant since there is no simple mechanism to explain this formation. A thermodynamic calculation for the reaction

$$Pb(^{3}P_{0}) + O_{2}(^{3}\Sigma) \rightarrow PbO + O \tag{1}$$

shows that the reaction is endothermic by 8497.2 cm^{-1} . Even if a substantial concentration of $Pb({}^{3}P_{2})$ is present under Boltzmann equilibrium conditions, the heat of reaction is exothermic by only 2009.1 cm⁻¹. This is not enough energy to excite PbO even to the a state, the least energetic excited state at 16024.9 cm⁻¹ above ground [2].

Based on the high pressure value for the activation energy for the reaction between Pb and $O_2(^3\Sigma)$ from table 1 (115.3 ± 22.4 kcal/mole) which is close to the dissociation energy of ground state oxygen [7], it is reasonable to suggest a two-step mechanism for the formation of PbO^{*},

$$Pb(g) + O_2(^{3}\Sigma) \rightarrow PbO(X) + O(^{3}P_2), \qquad (2)$$

$$Pb(g) + O(^{3}P_{2}) \rightarrow PbO^{*}.$$
(3)

Reaction (3) is exothermic by at least 33174.6 cm^{-1} . This energy is enough so that states as energetic as the D state [2] and possibly the E state [2] could be formed as a result of this reaction.

When the pressure is decreased, the activation energy also decreases. This decrease suggests a change in the reaction mechanism. It is possible that Pb is condensing to the solid according to the reaction scheme

$$Pb + Pb + M \rightarrow Pb_2 + M, \tag{4}$$

$$Pb_2 + Pb + M \rightarrow Pb_3 + M, \tag{5}$$

$$Pb_3 + Pb + M \rightarrow Pb_4 + M, \tag{6}$$

where M is a third body necessary to provide decreasing stabilization for the reaction [8]. It is known that, if the concentration of lead vapor exceeds the equilibrium saturated concentration by a factor of 50, then the condensation as shown in reactions (4)-(6), will occur [9]. Shock tube studies have shown that, in the temperature range of current interest after about 0.5 ms all the gaseous lead has condensed to small particles of solid [8]. If this type of condensation is occurring to an appreciable extent, then the mechanism of the reaction is expected to change. A four-center type of reaction occurring on the surface of the particles as shown in the reaction

$$Pb_{2}(g) + O_{2}(^{3}\Sigma) \rightarrow Pb...PbO + PbO^{*}$$
(7)

$$\vdots \quad \vdots$$

$$O...O$$

can be reasonably postulated.

The activation energy for this four-center type of reaction may be roughly approximated by taking the average of the two bond strengths or chemical dissociation energies, D_0 . Herzberg reports values of 16.4 kcal/mole for $D_0(Pb_2)$ and 117.1 kcal/mole for $D_0(O_2)$ [7]. The activation energy is thus 66.6 kcal/mole. The experimental activation energy from table 1 (63.9 ± 8.0 kcal/mole) is within experimental error of this value.

The exothermicity of reaction (7) is 20094.6 cm^{-1} for reaction with ground state Pb₂. This energy is large enough to produce PbO^{*} to the A state [2] and possibly to the C state [2] for reaction with excited Pb₂.

It is reasonable, thus, to postulate a combination of the two mechanisms shown to be operating under the experimental conditions described in this report. At higher pressures, reactions (2) and (3) predominate and at slightly lower pressures, reaction (7) predominates. Both mechanisms can produce PbO^{*}.

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