Flame Emission Studies of Ozone with Metal Alkyls: 
Zn \((\text{CH}_3)_2\) and Zn \((\text{C}_2\text{H}_5)_2\)

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Resolved flame emission spectra from the reaction of ozone, O\(_3\), with zinc dimethyl, Zn \((\text{CH}_3)_2\), and zinc diethyl, Zn \((\text{C}_2\text{H}_5)_2\), in a flow system at about one torr pressure reveal a number of interesting electronically-excited species. The Zn \((\text{CH}_3)_2\) + O\(_3\) flame has a pale blue appearance, characteristic of the "cool flame" bands of CH=O, while the Zn \((\text{C}_2\text{H}_5)_2\) + O\(_3\) flame has a deep blue appearance caused by ZnH\(^*\) emission. In addition the reaction of O\(_3\) with H atoms resulting probably from the decomposition of \(\text{C}_2\text{H}_5\) radicals in the latter reaction leads to strong OH \(\left(3^2\text{Π}_g\right)\) emission (Meinel bands). Also, OH\(^*\) \(\left(2^2\Sigma^+\right)\) emission is observed and is found to have a quadratic dependence on OH\(^+\). Mechanisms involving the different chemistry of CH\(_3\) and C\(_2\text{H}_5\) radicals in the flame are proposed to account for these observations.

I. Introduction
The gas-phase reactions of ozone with saturated and unsaturated hydrocarbons [1] have received rather careful attention from several workers interested in the general nature of combustion. Premixed [2, 3] and diffusion [4] flames of metal alkyl compounds have been carried out to determine such properties as ignition temperatures and burning velocities.

More recently, as part of a general intensive effort to develop electronic-transition chemical lasers, several groups [5-7] are again focusing their attention on the reactions of spontaneously flammable metal alkyl compounds with powerful oxidizers, notably ozone and fluorine. However, practically no attempt has been made to determine the mechanism of these reactions from the existing spectroscopic data. Although none of the emitting species produced in the gas-phase reactions studied so far have been shown to exhibit population inversions, we deem it necessary to investigate these reactions for we believe that the information thus gathered can shed new light not only on the nature of metal-alkyl reactions in particular, but also on the chemistry of combustion in general.

Flame studies are generally complicated by the background radiation associated with elevated temperatures and by the profuse number of chemical species present. Thus it would be advantageous to study the combustion of polyatomic molecules under single-collision conditions, i.e., at pressures below 1 mtorr. However, no visible emission from such reactions can be observed for the simple reason that most electronically-excited species can only result from secondary or even tertiary reactions.

There are also good reasons why one should turn to O\(_3\) as the oxidizing agent in these studies, but several workers [5, 6] have also found, in agreement with our own observations, that no chemiluminescence results from the reactions of O\(_3\) with spontaneously flammable fuels at pressures ca. 1 torr. Nor could emission be seen using N\(_2\)O as the oxidizer. Thus we chose to use O\(_3\) and to work at the minimum pressure at which emission sets in — about 0.5 torr in both reactions considered here.

II. Experimental
Figure 1 shows a schematic diagram of the experimental set-up. A glass sphere (125 cm\(^3\)) forms the...
reaction chamber. Four Pyrex "O" ring joints are
joined onto this sphere to house the viewing
windows and the flange for the reagent flow inlets.
A glass dewar of 350 cm$^3$ capacity is positioned
vertically on the glass sphere. An uncalibrated
thermocouple gauge (Veeco TG-7) monitors the
pressure 16 cm downstream from the reaction
zone. Further downstream, a larger glass dewar
of 750 cm$^3$ capacity traps most of the organic
reaction products. These dewars are cooled to
-78°C.

Diethyl zinc, obtained from Texas Alkyls, Inc.,
and dimethyl zinc, obtained from Alfa Products,
Inc., are used as received. Both vendors list
the purity of these compounds as greater than 98%.

Ozone is generated with a Welsbach (Model
T-408) ozonator and collected on silica gel cooled
to -78°C by a slurry of dry ice and acetone.
Immediately prior to the run, the ozone trap is
briefly opened to the pumps to remove excess
O$_2$.

The reaction chamber is initially pumped down
to less than 1 mtorr by a 1405B Welch pump
aided by a 3 in diffusion pump. The reactants are
introduced through two concentric glass nozzles
diameters 1.0 and 3.0 mm. The nozzles are
held by Cajon ultra-torr adapters onto the "O" ring
joint marked A in Fig. 1 which facilitates removal
for cleaning and depth adjustment during a run.
The metal alkyl compound, kept in a 20 cm$^3$ glass
cell, is introduced into the reaction region through
the outer nozzle at a pressure between 10 and 50
mtorr. Usually ozone is flowed in through the
inner nozzle, but the emission is independent of
the nozzle in which a reactant is introduced. To
ensure fairly complete combustion of the metal
alkyls, the pressure of ozone is maintained at about 0.8 to 1.0 torr, essentially equivalent to the total pressure in the reaction chamber.

The flame emission is spectrally resolved from 2800-8400 Å using a 1 m Interactive Technology Czerny-Turner spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. A Centronic S-20 photomultiplier (with extended red response) inside a cooled housing (~ -30°C) is attached to the exit slit of the spectrometer. The signal from the photomultiplier is detected by a Keithley 417 fast picoammeter whose output signal drives a Hewlett-Packard 7100B strip chart recorder. The latter provides a tracing of the spectrum.

When the metal alkyl is present in the reaction zone, emission is produced spontaneously as soon as ozone is introduced. During the entire scan of the emission, the flame has the appearance of a narrow horizontal luminous strip (jet) approximately 5 mm wide and 3 cm long. To avoid the complication of wall reactions we have made certain that the flame does not touch the reactor walls.

III. Results and Discussion

The flame from the reaction \( \text{O}_3 + \text{Zn(CH}_3)_2 \) has a pale blue color at a total pressure of about 1 torr. The diffusion flame from the reaction \( \text{O}_3 + \text{Zn(C}_2\text{H}_5)_2 \) is marked by a deep blue color as a result of intense emission of ZnH in the 4100-4300 Å region.

### A. \( \text{O}_3 + \text{Zn(C}_2\text{H}_5)_2 \) Reaction

Figure 2(a) shows the spectrum of the \( \text{O}_3 + \text{Zn(C}_2\text{H}_5)_2 \) chemiluminescence at about 1 torr pressure; the emitting species \( \text{Zn(aP}_1) \), \( \text{OH}^\dagger \) (2 Hi), and \( \text{ZnH(2 II)} \) are readily identified.

Early studies on the reactions of \( \text{Zn(CH}_3)_2 \) with \( \text{O}_2 \) at torr pressures [8-10] show that the reaction product has the approximate composition \( \text{Zn(CH}_3)_2 \cdot 2\text{O}_2 \). We can only speculate on the primary steps of these reactions, the initial step most probably involving the attack of the oxidizer \( \text{O}_2 \) or \( \text{O}_3 \) on the central zinc atom. If such is the case, the result could be the insertion of an O atom between a Zn-C bond or the rupture of the latter to form \( \text{ZnC}_2\text{H}_5 \).

1. **Acetaldehyde Emission**

   The broad emission band from 4350-4700 Å shows some diffuse vibrational structure (Fig. 3) and the emitter is believed to be due to acetaldehyde. The energy required to excite this species to the \( \text{A} \) state, about 82 kcal/mole, can amply be supplied through the exothermic reactions

   \[
   \text{CH}_3\text{CH}_2\text{O}^\cdot + \cdot\text{OH} \rightarrow \text{CH}_3\text{CHO}^\ast + \text{H}_2\text{O}, \tag{1}
   \]

   and

   \[
   \text{CH}_3\text{CH}_2\text{O}^\cdot + \text{CH}_3\text{CH}_2\text{O}^\cdot \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHO}^\ast. \tag{2}
   \]

We have no direct evidence of the species \( \text{CH}_3\text{CH}_2\text{O}^\cdot \) being present in the flame. However, there is evidence that the cool flame bands of \( \text{CH}_3\text{O} \) in other flames come from an analogous mechanism \([11]\).

2. **OH \((^2\text{II})\) Meinel Bands**

   The well-resolved bands from 5600 to 8400 Å, shown in Fig. 4, are definitely caused by emission from OH \((^2\text{II})\). The large doublet splittings are easily resolved using 500μm spectrometer slits, corresponding to a spectral resolution of about 5 Å. From analysis of the intensities of these bands, we see that \( \nu = 9, 8, \) and 7 are preferentially populated. This suggests that OH\(\dagger\) is produced in the following reaction \([12-13]\):

   \[
   \text{H} + \text{O}_3 \rightarrow \text{O}_2 + \text{OH}^\dagger (\nu=8,9); \Delta\text{H}= -77\text{kcal/mole}. \tag{3}
   \]

   The likely source of H atoms is the decomposition of \( \text{C}_2\text{H}_5 \) radicals to yield ethylene (\( \text{C}_2\text{H}_4 \)) and H.

3. **OH \((^2\Sigma\text{)}\) and Zn \((^3\text{P}_1)\)**

   Although the OH bands from 3000 to 3080 Å are completely obscured by the intense Zn line(Fig. 5), we can nonetheless obtain a fairly good estimate of the OH rotational temperature by examining the well-resolved P branch of the (0,0) band lying between 3100 and 3300 Å. Our analysis shows \( T_{\text{rot}} \) to be 2000-2200K (Fig. 6). This value is well below that reported by Benson, et al. \([6]\) from studies of \( \text{F}_2/\text{O}_2 + \) metal alkyl flames, where they measure \( T_{\text{rot}} \) of OH to be \( \approx 4000\text{K} \). It is well
known that flames with \( \text{F}_2 \) as the oxidizer tend to yield higher rotational temperatures [14].

The very intense Zn intercombination line \((^3P_1 - ^1S_0)\) at 3076 Å may arise from several mechanisms:

\[
H + H + \text{Zn} \rightarrow \text{Zn} \left(^3P_1\right) + \text{H}_2, \tag{4}
\]

\[
H + \text{OH} + \text{Zn} \rightarrow \text{Zn} \left(^3P_1\right) + \text{H}_2\text{O}, \tag{5}
\]

\[
\text{OH} \left(^2\Sigma^+\right) + \text{Zn} \left(^1S_0\right) \rightarrow \text{OH} \left(^3\Pi\right) + \text{Zn} \left(^3P_1\right). \tag{6}
\]

The three-body recombinations given in (4) and (5) have been shown by Padley and Sugden [15] to account for the nonthermal excitation of a great number of metal atoms in their flame studies. However, we speculate that (6) may be an important mechanism here because of the close coincidence between the energy levels of the species involved.

The emission of OH in the ultraviolet region has been observed in almost all types of hydrocarbon combustion. Gaydon [16] has suggested the following reaction to account for these observations:

\[
\text{CH} + \text{O}_2 \rightarrow \text{CO} + \text{OH}^* \left(^2\Sigma^+\right); \Delta H = -160 \text{ kcal/mole.} \tag{7}
\]

Under our operating conditions it is very unlikely that CH could be formed abundantly from the
decomposition of $\text{C}_2\text{H}_5\cdot$ or from subsequent reactions. Therefore, an alternative mechanism must be sought. The observation of $\text{OH}(^2\Sigma^+)$ emission in the reaction of $\text{H}$ with $\text{O}_3$ has been reported [17, 18]. In his flame study of this reaction at 0.5 to 4.5 torr pressures, Broida [17] finds that the intensity of the ultraviolet radiation ($A^2\Sigma^+ - X^2\Pi_j$) depends upon the square of the intensity of the visible $\text{OH}^1(^2\Pi_j)$ radiation. Following his procedure, we have plotted the intensity of the (0, 0) $Q_2$ head of $\text{OH}(^2\Sigma^+)$ at 3089 Å as a function of the intensity of the $\text{OH}^1(^2\Pi_j)$ (9-4) head at 7756 Å. The brightness of the flame is varied by changing the $\text{Zn(C}_2\text{H}_5)_2$ flow slightly at a total reaction chamber pressure of about 1 torr, while maintaining the $\text{O}_3$ flow constant. We choose the $Q_2$ head at 3089 Å rather than the $R_1$ head at 3064 Å because the latter peak is completely obscured by the intense $\text{Zn}$ line. The result shown in Fig. 7 reveals qualitatively a square dependence of $\text{OH}(^2\Sigma^+)$ on $\text{OH}(^2\Pi_j)$. A similar relationship is obtained when the $\text{O}_3$ flow is varied while the $\text{Zn(C}_2\text{H}_5)_2$ flow is maintained constant.

4. $\text{ZnH}(^2\Pi)$

The spontaneous production of $\text{ZnH}(^2\Pi)$ in the reaction of $\text{O}_3$ with $\text{Zn(C}_2\text{H}_5)_2$ was a great surprise to us. Although $\text{ZnH}$ emission has been observed by Egerton and Rudrakanchana [4] in a diffusion flame of $\text{O}_2 + \text{Zn(CH}_3)_2$ at several torr pressures, the emission of metal hydrides from diffusion flames is still considered rare.

An analogous process involving $\text{HgH}$ has been documented by Gaviola and Wood [19] and by Beutler and Rabinowitz [20]. By exciting the $\text{Hg}$ atoms in a mixture of $\text{Hg}$ vapor and $\text{H}_2$, these workers found the initial reactions to be

$$\text{Hg}^* + \text{H}_2 \rightarrow \text{Hg} + \text{H} + \text{K.E.} \quad (8)$$

$$\text{Hg}^* + \text{H}_2 \rightarrow \text{HgH} + \text{H} + \text{K.E.} \quad (9)$$

Reaction (9) was deduced from the observation of $\text{HgH}$ emission via sensitized fluorescence:

$$\text{Hg}^* + \text{HgH} \rightarrow \text{HgH}^* + \text{Hg} \quad (10)$$
In the reaction of \( \text{O}_3 \) with \( \text{Zn}(\text{C}_2\text{H}_5)_2 \), the strong emission from \( \text{OH}^\dagger (^2\Sigma\) suggests a fair excess of \( \text{H} \) atoms [See reaction (3)]. The intense Zn emission implies that there is also a relatively high concentration of \( \text{Zn}^\ast \) atoms. The following reactions therefore suggest themselves for the formation of \( \text{ZnH}^\ast \):

\[
\text{Zn}^\ast (^3P_1) + \text{H}_2 (^1\Sigma) \rightarrow \text{ZnH} (^2\Sigma) + \text{H}(^2S), \tag{11}
\]

\[
\text{ZnH} (^2\Sigma) + \text{Zn}^\ast (^3P_1) \rightarrow \text{ZnH}^\ast (^2\Pi) + \text{Zn}(^1S_0), \tag{12}
\]

or \( \text{Zn}^\ast (^3P_1) + \text{H}(^2S) + \text{M} \rightarrow \text{ZnH}^\ast (^2\Pi) + \text{M}. \tag{13} \)

B. \( \text{O}_3 + \text{Zn}(\text{CH}_2)_2 \)

This reaction should parallel that of \( \text{O}_3 + \text{Zn} (\text{C}_2\text{H}_5)_2 \), the initial step probably involving the attack of \( \text{O}_3 \) on the central \( \text{Zn} \) atom. Figure 2(b) shows the chemiluminescence observed. The species responsible for the emission in the region 3700–4500 Å is readily identified as formaldehyde (\( \text{CH}_2\text{O} \)). In sharp contrast to the reaction of \( \text{O}_3 \) with \( \text{Zn}(\text{C}_2\text{H}_5)_2 \), there is no emission from \( \text{Zn} \), \( \text{ZnH} \), or \( \text{OH} \). We believe this is a consequence of the fact that no significant concentrations of \( \text{H} \) atoms are produced. We attribute this to the different chemical fates of \( \text{CH}_2 \) and \( \text{C}_2\text{H}_5 \) radicals in the flame.

The cool flame bands of formaldehyde reflect a low flame temperature and are usually associated with the breakdown of peroxides in flames. The lowest excited state of \( \text{CH}_2\text{O} \) requires about 81 kcal/mole for activation. This energy is amply supplied \([11]\) via a reaction analogous to (2)

\[
\text{CH}_3\text{O} \cdot + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{O}^\ast + \text{CH}_3\text{OH};
\]

\[
\Delta H = -96 \text{ kcal/mole}. \tag{14}
\]
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Fig. 5. Some rotational lines of OH, $A^2\Sigma^+ - X^2\Pi_i$, (0, 0) band from the reaction of ozone with Zn(C₂H₅)₂. Note how the intense Zn intercombination line (3076 Å) has obscured the $R_1$ head at 3064 Å.

This appears to account for the observed emission.

IV. CONCLUSION

By postulating the initial combustion step of Zn(CH₃)₂ and Zn(C₂H₅)₂ as the attack of the central Zn atom by O₃, we can see that the resultant flame spectra are markedly different because of the dissimilar chemistry of C₂H₅ and CH₃ radicals in the flame. In the O₃ + Zn(C₂H₅)₂ system, there is a significant concentration of H and OH; by contrast, the O₃ + Zn(CH₃)₂ system probably yields methoxy radicals as major primary products.

We are extending these investigations to other metal alkyl compounds and we have already observed quite dissimilar behavior for the combustion of metal organics when the organic moiety is methyl or ethyl.

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Fig. 7. The intensity of the $Q_2$ head for the (0, 0) band of the OH $A^2Σ^+ - X^2Π_v$ system is plotted as a function of the square of the intensity of the OH (9-4) $^2Π_v$ transition. The intensities are measured from the O$_3^+$ Zn(C$_2$H$_5$)$_2$ flame at a total pressure of one torr.

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