

# Chemiluminescence in the Reactions of Ozone

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## I. Introduction

In an exothermic chemical reaction the products carry off excess energy in translational, rotational, vibrational, or electronic form. When a portion of the excess energy is emitted as infrared, visible, or ultraviolet light the reaction is referred to as chemiluminescent. The study of chemiluminescence (CL) dates back more than three centuries when the glow accompanying the oxidation of phosphorus was investigated by Hennig Brand and Robert Boyle.

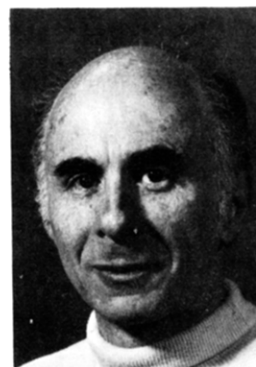
The field is a very active one and there have been a considerable number of recent reviews on chemiluminescence<sup>1-5</sup> and bioluminescence.<sup>3,5-7</sup>

CL induced by ozone was observed in 1896 when ethanol was oxidized by ozone.<sup>8</sup> And some 40 years later it was claimed (correctly) that ultraviolet light was emitted when ozone reacts with hydrogen sulfide.<sup>9</sup> In point of fact, nearly all of the gas phase reactions of ozone are chemiluminescent. The range of wavelengths emitted is at least from 250 nm ( $O_3 + C_2F_4 \rightarrow h\nu$ ) to 2500 nm ( $O_3 + NO \rightarrow h\nu$ ).

Initially sparked by the interest in atmospheric chemistry, a large number of chemiluminescent ozone reactions have been discovered in the last few years. There has been no review of these reactions other than a brief survey in the review of gas-phase CL by Campbell and Baulch<sup>4</sup> which covered publications up to mid-1977. This Review will take that date as the starting point for most gas-phase reactions. Liquid- and solid-phase ozone CL will also be considered and coverage has been attempted to early 1984.

## II. Properties and Hazards of Ozone

Ozone,  $O_3$ , is a ground state singlet molecule which is deep blue in the solid and liquid states. The gas has a strong absorption in the ultraviolet region ( $\epsilon_{\max} = 3004 \pm 45 \text{ M}^{-1} \text{ cm}^{-1}$  at 273 K) which is conveniently close to the 254-nm line of mercury arcs. At this wavelength a detector which can measure a decrease of 1% of incident light has a corresponding sensitivity of about 1 mTorr of ozone. Ozone also has a weak absorption band in the visible and this has been utilized by using a light emitting diode ( $\lambda_{\max} = 584 \text{ nm}$ ) as the monitoring source.<sup>10</sup>



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Ozone is usually made by passing  $O_2$  through an electrical discharge and such ozonized oxygen is not in itself hazardous. The reaction of ozone with many substrates leads to ozonides or peroxides, many of which are explosively unstable.<sup>11,12</sup> Conjugated dienes even at  $-78^\circ \text{C}$  can combust violently when a stream of ozonized oxygen is passed.<sup>13</sup> Gas-phase chemiluminescent reactions at room temperature and above do not normally produce ozonides.

Ozonized oxygen typically contains several percent of ozone but molecular oxygen is reactive and for many studies pure ozone or ozone in an inert diluent is needed. The hazardous nature of pure ozone has been described.<sup>14,15</sup> The solid is relatively safe but liquid ozone can detonate and since the melting point of ozone is  $-193^\circ \text{C}$  liquid ozone is formed within a few seconds of removal of liquid nitrogen from a cooled container of the solid. In the author's laboratory pure ozone is routinely thawed and refrozen in milligram quantities but only allowed to mix with substrates in the gas phase. Larger quantities of ozone may be handled by adsorption on silica gel at  $-78^\circ \text{C}$ <sup>12,16</sup> with precautions to ensure that the temperature does not fall appreciably below  $-100^\circ \text{C}$  so that liquid ozone does not form.<sup>17</sup>

Pure gaseous ozone at a few torr at room temperature is kinetically stable. The theoretical decomposition rate of 1 atm of pure ozone at 298 K is only 0.2% per year

but impurities and surface reactions lead to chains which make ozone at high pressures a potential hazard. Methods have been described, however, for stabilizing the gas at high pressures.<sup>18</sup>

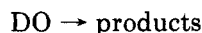
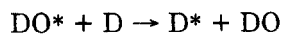
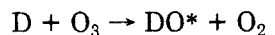
### III. Ozone Chemiluminescence in Condensed Phases

In the liquid phase chemiluminescent spectra are usually similar to fluorescence spectra under the same conditions. Typically, they are broad and virtually structureless because of rapid vibrational deactivation by the solvent. Liquid-phase CL is easy to produce and tubes that will glow for hours are commercially available due mainly to the work of Rauhut.<sup>2</sup> The most efficient luminescers are formed by the decomposition of four-membered ring cyclic peroxides, in particular the 1,2-dioxetanes<sup>19</sup> and 1,2-dioxetanones.<sup>20</sup> When these substances decompose in the presence of efficient fluorescers, such as rubrene, quantum efficiencies for emission of >50% can be obtained. The superficially similar five-membered ozonides do not generally give similar efficient chemiluminescence. Although CL is typical of gas-phase ozone reactions it is less common in the liquid phase, perhaps because of the relative stability of the five-membered ozonides at lower temperatures.

Few direct comparisons of gas-phase and liquid-phase ozone reactions are possible but one example is the reaction of atomic hydrogen with ozone. In the gas phase the reaction  $\text{H} + \text{O}_3 \rightarrow \text{HO}(\text{X}^2\Pi_i, v \leq 9) + \text{O}_2$  emits the well-known Meinel bands in the infrared region.<sup>21</sup> The reaction is rapid, with  $k_{298} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . This reaction has been recently investigated in aqueous solution and the reported value of  $k_{298}$  was  $3.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  with no CL being noted, presumably because of rapid solution deactivation.<sup>22</sup>

Early work (1896–1941) on ozone-induced CL in the liquid phase has been summarized by Bernanose and Rene.<sup>23</sup> The work is largely qualitative and in some cases substrates of questionable purity were used.

The reactions of both hydrogen peroxide and of ozonized air on the dyes eosin and uranin were found to produce CL.<sup>24</sup> Emission spectra were affected by light absorption from the dye, but when very dilute dye solutions were employed the chemiluminescent spectrum was similar to the fluorescence spectrum of the dye. Several possible mechanisms were considered and the process of electronic activation is more complex than the energy transfer sequence

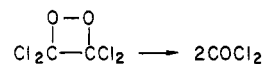


where  $\text{D}^*$  represents the excited singlet dye. The exact mechanism, however, is uncertain.

Bubbling ozonized air through solutions of aromatic aldehydes and polyacenes leads to CL with quantum yields for emission of the order of  $10^{-5}$ .<sup>25,26a</sup> This rises to  $10^{-3}$  in the case of fluorescein.<sup>25</sup> Ozone also gives CL with uranyl ion in acid solution.<sup>26b</sup>

When simpler molecules are used as substrate, the chemiluminescent spectra can be identified with prod-

uct rather than reactant, which gives an insight into the mechanism of ozone attack. Sulfur in  $\text{H}_2\text{SO}_4$  solution is attacked by ozone to give triplet-excited  $\text{SO}_2$  emission.<sup>27</sup> And when ozone was bubbled through chloroform an emission ascribed to electronically excited phosgene was seen.<sup>28</sup> It was postulated that the pathway was via the 1,2-dioxetane



analogous to the chemiluminescent reactions of hydrogen peroxide with alkenes.<sup>19</sup>

Both peroxides<sup>29</sup> and singlet molecular oxygen ( $^1\Delta_g$ )<sup>30</sup> have been extensively reacted with dyes and other aromatic fluorescers to produce CL which is identical to the dye fluorescence. Single-step activation did not provide sufficient energy to account for the observed emission and in both cases energy pooling was postulated. Interestingly,  $\text{O}_2(^3\Sigma_g^-)$  was found to have a strong quenching effect on the emission<sup>30</sup> which suggests that ozonized oxygen is not a good chemiluminescer in these systems.

Before leaving the topic of liquid-phase ozonization it is worth pointing out that the common practice of bubbling ozonized oxygen through a reactive solution, while synthetically useful, is only of qualitative value from a kinetic viewpoint. The system has three drawbacks: (1) the reaction volume is undefined, (2) the reaction phase is uncertain, and (3) the oxygen diluent is not inert. Far preferable would be the reaction with dissolved ozone in homogeneous solution as has been carried out in the reaction with tetrafluoroethene.<sup>31</sup>

There is little in the recent literature on the chemiluminescent interaction of ozone and solids although some older work has been reported.<sup>23</sup> Many solid surfaces catalyze the decomposition of ozone and these heterogeneous systems have been recently studied but no light emission has been reported.<sup>32,33</sup> On the other hand, the exposure of  $\text{O}_2$  to a pure silicon surface has been observed to be chemiluminescent.<sup>34</sup>

An extensive but qualitative investigation showed that light was emitted when ozone came in contact with a large number of organic chemicals both in solution and in the solid state.<sup>35</sup> Similarly, light is emitted when ozone comes in contact with dyes adsorbed on a solid support<sup>36</sup> and with paper impregnated with various substances.<sup>23,37a</sup> These studies will be considered shortly from the point of view of analytical applications.

### IV. Analytical Applications

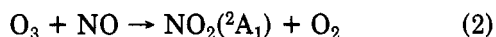
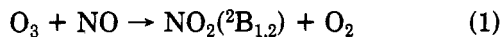
A chemiluminescing system has an inherently low background and with a suitable light sensor can serve as a detector of high signal-to-noise ratio, especially if cooled photomultipliers and photon counting techniques are used. These advantages overcome the relatively low quantum yields found in most ozone-CL systems. Ozone detectors based on CL have been available since 1971 and sensitivities claimed have improved to the parts per billion range.

Several different types of chemiluminescing systems form the basis of these commercial instruments and examples of methods which have been used are as follows. Ozone gives CL when in contact with a fresh aluminum surface and this has been provided by a moving tape (Pollution Monitors, Inc., Chicago, IL).

The well-known reaction between ozone and gaseous ethylene has formed the basis for other commercial detectors (REM Inc., Santa Monica, CA; Columbia Scientific Industries Corp., Austin, TX). Ozone dissolved in water has been measured by an unspecified liquid-phase chemiluminescent reaction (OREC, Phoenix, AZ). A nitrogen analyzer has been described which oxidizes the combined nitrogen to nitric oxide. Nanogram quantities of combined nitrogen can be detected (Antek Instruments, Inc., Houston, TX) by using the reaction  $O_3 + NO \rightarrow O_2 + NO_2 + h\nu$ .

Another method which can be used for ozone detection is the measurement of CL produced when ozone contacts paper impregnated with a variety of organic compounds.<sup>23</sup> Even paper soaked in common lubricating oil provides a system which, using photon counting, can give a sensitivity of  $\sim 1$  ppb of ozone!<sup>37a</sup>

One extremely useful aspect of CL is its use as a method of measuring ozone levels in the stratosphere. In early experiments nitric oxide was released from rockets at high altitudes and the resultant glow measured from the ground. The reaction between  $O_3$  and NO occurs via two channels:



At room temperature 93% of the  $NO_2$  is formed vibrationally excited in the ground ( $^2A_1$ ) electronic state. Subsequent decay of these states produces emission from 600 to at least 3000 nm. However, the reaction between O atoms and NO also produces electronically and vibrationally excited  $NO_2$ , which complicates the monitoring of  $O_3$  in the stratosphere. The problem was solved by using a solid dye which chemiluminesced on exposure to ozone and removing O atoms with an inlet tube to the interior of the rocket or balloon probe. CL from the  $O_3$ /dye system is specific and can be recorded or transmitted from the stratosphere probe. Stable and sensitive results were obtained by allowing rhodamine B to adsorb on porous borosilicate glass. When this combination is exposed to ozone, light is emitted across a broad band with a maximum at about 580 nm. In this manner Hilsenrath and Kirschner<sup>36</sup> were able to detect stratospheric ozone down to  $5 \times 10^8$  molecule  $cm^{-3}$ , which corresponds to 0.02 ppb in a standard atmosphere.

The detection of NO and  $NO_2$  at the parts-per-trillion level (ppt) has been reported using  $O_3$  CL. Sensitivities claimed were 5 ppt for NO and 10 ppt for  $NO_2$ , using a photolytic converter.<sup>37b</sup> The  $O_3$ /NO system has been shown to give an additional emission with a peak near 800 nm as a result of electronically excited  $O_2$  giving rise to vibrationally excited  $O_3$ .<sup>37c</sup>

Unsurprisingly, ozone CL has been exploited as a detector in gas chromatography for unsaturated hydrocarbons and for sulfur-containing compounds.<sup>38</sup>

Ozone CL has also been investigated as an analytical tool for the detection of the following elements and compounds.

**Arsenic.** Fujiwara et al.<sup>39</sup> used sodium borohydride to reduce arsenic compounds to  $AsH_3$  which was then reacted with ozonized oxygen. The subsequent CL resulted in a system with a sensitivity of 0.15 ng of As, corresponding to 0.003 ppb for a 50-mL sample. They obtained much lower sensitivity (10 ng) with Sb. This

disagrees with the work of Stedman et al.<sup>40</sup> who, using a similar technique, obtained a sensitivity of 0.2 ng of As and a comparable value for Sb, which would thus be a potential interferent. Nevertheless, both groups demonstrated the same high sensitivity of  $O_3$  CL as a detector for As with advantages over the atomic absorption spectroscopy usually employed.

**Tin, Antimony, and Selenium.** Tin, antimony, and selenium hydrides were synthesized by using borohydride reduction techniques and were reacted with  $O_3$ . Reported sensitivities were 35, 10, and 110 ng for Sn, Sb, and Se, respectively. Bismuth and mercury formed hydrides but gave nonlinear results and lead, germanium, and tellurium did not give CL under the conditions used.<sup>39</sup>

**Nickel Carbonyl.** This important industrial compound is highly toxic and is considered carcinogenic. A threshold limit value for this compound has been set at 1 ppb and thus a sensitive detection method is of great value. Stedman et al. have developed an  $O_3$  CL detector which comes close to the required sensitivity.<sup>41,42</sup> Interference from NO chemiluminescence was ingeniously reduced by using a pulsed CO flow, which increases CL from carbonyls but has no effect on CL from NO. Since commercial CO contains carbonyls as an impurity, it was important to remove the carbonyls and this was done with an iodine/charcoal trap.<sup>42</sup> The interference from NO and from iron pentacarbonyl was further reduced by Houpt, Van der Waal, and Langeweg by using optical filters and modifying the flow system.<sup>43</sup>

**Sulfur Compounds.** Ozone attacks compounds containing reduced sulfur producing eventually electronically excited sulfur dioxide via the sequence  $SO + O_3 \rightarrow SO_2^* + O_2$ . An investigation of the CL from the reaction of  $O_3$  with hydrogen sulfide, dimethyl sulfide, methyl mercaptan, and thiophene gave detection limits of 4, 0.3, 0.1, and 12 ppb, respectively.<sup>44</sup> Some interference from ethylene CL was noted and the method cannot discriminate between the sulfur compounds since the emitter is common. It is interesting to note that an increase in CL was sometimes found when ozonized air rather than ozonized oxygen was used and this increase was ascribed to the presence of nitrogen oxides formed in the ozonizer.

## V. Spectroscopy of Reactive Intermediates

Ozone CL has been important in the spectroscopy of reactive intermediates both in the discovery of new emitting species and also in the confirmation of the source of spectra produced in ill-defined systems. For example, trace impurities can cause strong emissions because of the short radiative lifetimes of many electronic states and the high sensitivity of the detectors used. Thus, CN bands are often seen in the reactions of O atoms with hydrocarbons because of N atom impurity. Similarly, CO bands often accompany the reaction of F atoms with hydrocarbons because of the  $O_2$  impurity in commercial  $F_2$ .<sup>45</sup> With ozone-containing systems it has been possible to produce electronically and vibrationally excited intermediates under mild conditions free of the ambiguities sometimes associated with discharged gases.

**Oxides of Group 5 Elements.** As previously mentioned, the reaction between nitric oxide and ozone

TABLE I.<sup>a</sup> Spectral Assignments

system	band	assignment	transition
PH <sub>3</sub> /O <sub>3</sub> /O <sub>2</sub>	continuum, 380–800 nm	PO <sub>2</sub> <sup>b</sup>	<sup>2</sup> B <sub>1</sub> → <sup>2</sup> A <sub>1</sub> <sup>c</sup>
AsH <sub>3</sub> /O/O <sub>2</sub>	244–270 nm	AsO	B <sup>2</sup> Σ <sup>+</sup> → X <sup>2</sup> Π
	295–345 nm	AsO	A <sup>2</sup> Σ <sup>+</sup> → X <sup>2</sup> Π
	continuum, 350–700 nm	AsO <sub>2</sub> <sup>b</sup>	<sup>2</sup> B <sub>1</sub> → <sup>2</sup> A <sub>1</sub> <sup>c</sup>
AsH <sub>3</sub> /O <sub>3</sub> /O <sub>2</sub>	295–345 nm	AsO	A <sup>2</sup> Σ <sup>+</sup> → X <sup>2</sup> Π
AsH <sub>3</sub> /O <sub>3</sub> /N <sub>2</sub>	continuum, 360–700 nm	AsO <sub>2</sub> <sup>b</sup>	<sup>2</sup> B <sub>1</sub> → <sup>2</sup> A <sub>1</sub> <sup>c</sup>
SbH <sub>3</sub> /O <sub>3</sub> /O <sub>2</sub>	340–450 nm	SbO	B <sup>2</sup> Σ <sup>+</sup> → X <sup>2</sup> Π <sub>1/2</sub>
			B <sup>2</sup> Σ <sup>+</sup> → X <sup>2</sup> Π <sub>3/2</sub>
	450–680 nm	SbO	A <sup>2</sup> Π <sub>1/2,3/2</sub> → X <sup>2</sup> Π <sub>1/2,3/2</sub>

<sup>a</sup> Reprinted with permission from ref 49. Copyright 1983, The Royal Society of Chemistry, London. <sup>b</sup> Conclusive identification of these emitting species has yet to be made. <sup>c</sup> By analogy with NO<sub>2</sub>.

produces vibronically and vibrationally excited NO<sub>2</sub> (eq 1 and 2). The chemiluminescence of this reaction was discovered in 1949<sup>46</sup> and the spectroscopy is reasonably well-known.<sup>47,48</sup> Aspects of the dynamics of the reaction will be mentioned later.

The spectroscopy of the emissions obtained in the reactions of ozone with phosphine, arsine, and stibine have been investigated in detail by Stedman et al.<sup>40,49</sup> The mechanisms, to be discussed later, are extremely complex and in the case of arsenic and antimony, a variety of emitters was identified. Phosphorus gave only a continuum in the range 380–800 nm which was tentatively assigned to PO<sub>2</sub>(<sup>2</sup>B<sub>1</sub> → <sup>2</sup>A<sub>1</sub>). This is the same emission seen in the oxidation of phosphorus by moist air. The spectra observed by Fraser and Stedman<sup>49</sup> in the reactions of AsH<sub>3</sub> with O<sub>3</sub> in an O<sub>2</sub> diluent, with O<sub>3</sub> in a N<sub>2</sub> diluent, and with O atoms in an O<sub>2</sub> diluent are shown in Figure 1. Their spectral assignments for the group 5 oxides are given in Table I.

**HSO and SO<sub>2</sub> Emission.** The reaction of ozone with a variety of gaseous sulfides produces emission from electronically excited sulfur dioxide from the reaction SO + O<sub>3</sub> → SO<sub>2</sub>(A<sup>1</sup>B<sub>1</sub>) + O<sub>2</sub>, giving a pseudo-continuum with a maximum intensity at about 360 nm.<sup>50</sup> Collisional population of the  $\tilde{a}^3B_1$  state gives, in the absence of quenchers, triplet emission which consists of superimposed bands in the range 370–450 nm.<sup>51,52a,b</sup> Vibrationally resolved phosphorescence was obtained in the reaction between ozone and methyl mercaptan by using a beam-gas apparatus and adding controlled amounts of helium to produce triplet SO<sub>2</sub>.<sup>53</sup> In the case of the reaction with thiirane, evidence for a long-lived metastable state of SO<sub>2</sub> was obtained.<sup>54</sup>

The HSO radical was first clearly identified as a result of the CL from the reaction of O<sub>3</sub> with H<sub>2</sub>S.<sup>51</sup> In addition to the SO<sub>2</sub> bands at shorter wavelengths, a series of well-resolved progressions from 520 to 960 nm is emitted which further work assigned to the <sup>2</sup>A'–<sup>2</sup>A'' transition.<sup>55a</sup> Recent papers have described the laser fluorescence of HSO produced by the reaction of discharged O<sub>2</sub> with sulfur compounds.<sup>55b</sup>

**Metal Oxides.** The production of electronically excited metal oxides by the reaction of ozone with beams of evaporated metal atoms, O<sub>3</sub> + M → MO\* + O<sub>2</sub>, has been reviewed by Campbell and Baulch.<sup>4</sup> In some cases new states were found; in other cases large, vibrational extensions of previously known states were observed in emission. Examples of such new states are CaO(A<sup>1</sup>Π),

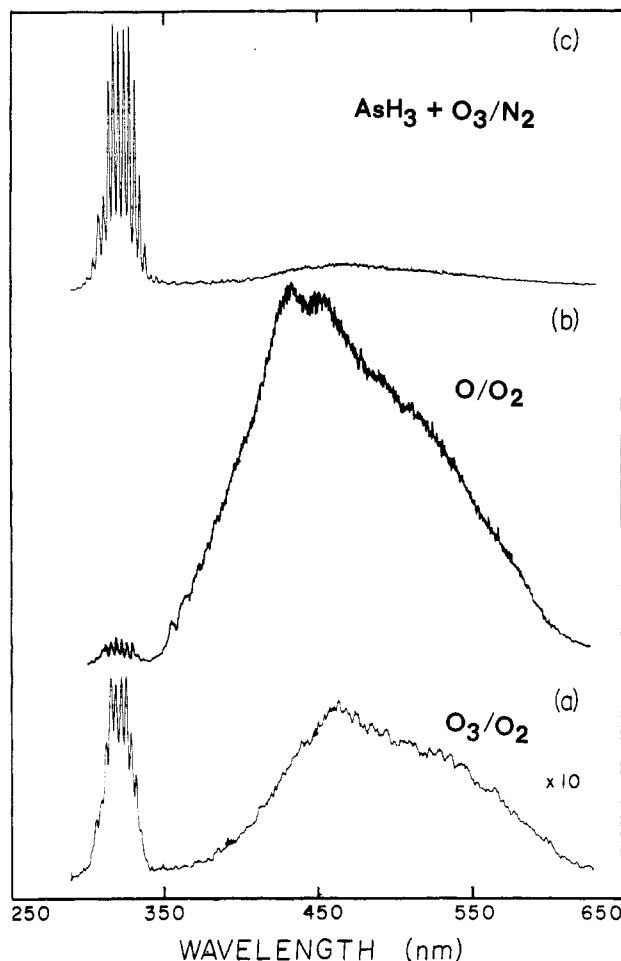


Figure 1. (a) AsH<sub>3</sub> + O<sub>3</sub>/O<sub>2</sub> Spectrum. An uncorrected photoelectric spectrum obtained from the chemiluminescence generated by mixing 14.2 cm<sup>3</sup> min<sup>-1</sup> of 6.8% AsH<sub>3</sub> in N<sub>2</sub> with 500 cm<sup>3</sup> min<sup>-1</sup> of 3.1% O<sub>3</sub> in O<sub>2</sub> at a total pressure of 1.9 Torr. (b) AsH<sub>3</sub> + O<sub>3</sub>/N<sub>2</sub> Spectrum. Uncorrected photoelectric spectrum obtained from the chemiluminescence generated by mixing 6.7 cm<sup>3</sup> min<sup>-1</sup> of 6.8% AsH<sub>3</sub> in N<sub>2</sub> with 620 cm<sup>3</sup> min<sup>-1</sup> of 2.63% O<sub>3</sub> in N<sub>2</sub> at a total pressure of 2 Torr. (c) AsH<sub>3</sub> + O/O<sub>2</sub>. Uncorrected photoelectric spectrum obtained from the chemiluminescence generated by mixing 9.2 cm<sup>3</sup> min<sup>-1</sup> of 6.8% AsH<sub>3</sub> in N<sub>2</sub> with 650 cm<sup>3</sup> min<sup>-1</sup> of discharged oxygen at a total pressure of 2 Torr. The spectrum in 1a was a factor of 10 less intense than 1b and 1c and is shown on an expanded scale. Reprinted with permission from ref 49. Copyright 1983, The Royal Society of Chemistry, London.

SrO(A<sup>1</sup>Π), PbO(a<sup>3</sup>Σ<sup>+</sup>, b<sup>3</sup>Σ<sup>+</sup>), ScO(C<sup>2</sup>Π), YO(C<sup>2</sup>Π), and FeO(C<sup>1</sup>). More recent work has extended previous analyses of the AlO(A<sup>2</sup>Π, B<sup>2</sup>Σ<sup>+</sup>) and BaO(A<sup>1</sup>Σ<sup>+</sup>, D<sup>1</sup>Σ<sup>+</sup>) states.<sup>56a,b</sup> The previously discussed emission from the reaction of O<sub>3</sub> with nickel carbonyl has been identified as due to excited nickel oxide probably from the reaction Ni + O<sub>3</sub> → NiO\* + O<sub>2</sub>.<sup>41,42</sup>

**Emission from the Reaction of Ozone with Organic Compounds.** Of the recent work on CL of O<sub>3</sub> with organic compounds, the most extensive is the work of Pitts and co-workers who investigated the reactions of O<sub>3</sub> with simple and halogenated alkenes, cyclic alkenes, dialkenes, alkynes, and alkenals. In addition, experiments with deuterated species were reported and quantum yields were measured.<sup>57,58</sup> The results of these and other investigations are summarized in Table II. Not all species are formed under all conditions: some emissions are strongly pressure dependent and others depend to some extent on whether O<sub>2</sub> is present or not. Nevertheless, the table gives an indication of the ubi-

TABLE II. Emission from Alkenes and Related Compounds with Ozone

substrate	emitter/state						other	ref
	OH/XII <sub>i</sub>	OH/A <sup>2</sup> Σ <sup>+</sup>	CH/ <sup>2</sup> Δ	CFO/-	CH <sub>2</sub> O/ <sup>1</sup> A	αDK <sup>o</sup> / <sup>3</sup> A <sub>u</sub>		
ethylene	X	X			X			57
acetylene	X	?	X				CHO	57, 58
propene	X	X			X	gl		57, 59
1-butene	X				X	gl		57, 59
isobutene	X	X			X	Megl		57, 59
3-methyl-1-butene	X				X	gl		58
cis-2-butene	X	X			X	gl		57, 59
trans-2-butene	X				X	gl		57, 59
2-methyl-2-butene	X				X	Megl		57, 59
2,3-dimethyl-2-butene	X				X	Megl		57, 59
trans-3-hexene	X				X	X		58
trans-4-octene	X	X			X	X		58
allene	X	X	X		X			58
1,3-butadiene	X	X			X	?		58
cyclopentene	X	X			X	gl		58
cyclohexene	X				X	gl		59
benzene	X	X	X			X		63
toluene	X	X	X			X		63
<i>o</i> -, <i>m</i> -, <i>p</i> -xylene	X	X	X			X		63
1,1-difluoroethene		X		?				58
cis-1,2-difluoroethene	X	X		X				58, 61
trans-1,2-difluoroethene	X	X		X				58, 61
trifluoroethene				X			CF <sub>2</sub>	61
chlorotrifluoroethene				X				61
tetrafluoroethene							CF <sub>2</sub>	60
3,3,3-trifluoropropene	X	X						58
1,1-dichloropropene	X	X			X	?		
monoterpenes	X				X	Megl		62a,b
propenal	X	X			X	gl	CO <sub>2</sub> ?	58
2-butenal	X	X			?	gl	CO <sub>2</sub> ?	58

<sup>a</sup> α-Diketones: gl = glyoxal; Megl = methylglyoxal.

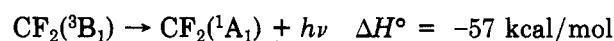
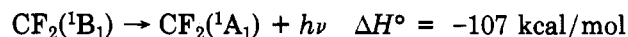
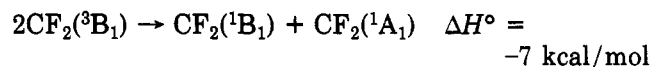
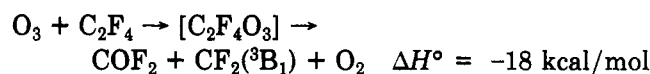
quity and complexity of chemiluminescence in systems of unsaturated compounds. Some of the species, such as CFO and CF<sub>2</sub>(<sup>1</sup>B<sub>1</sub>), were seen in gas-phase emission for the first time by using ozone chemiluminescent systems.

## VI. Kinetics and Mechanism

The use of CL as a tool in mechanistic studies has two important potentialities. First, it offers the opportunity of identifying reactive intermediates, sometimes for the first time, and of measuring their properties. Second, the wavelengths emitted specify an energy requirement which reduces and sometimes eliminates ambiguity in the choice of possible mechanisms. There is a concomitant risk in overdependence on CL: it is so easily detectable that it may encourage the researcher to spend much time investigating kinetically unimportant reaction pathways.

**Effect of an O<sub>2</sub> Diluent.** As mentioned earlier, molecular oxygen is far from inert in many systems and it may have a large effect on CL. O<sub>2</sub> was found to increase the intensity of CH<sub>2</sub>O(<sup>1</sup>A<sub>2</sub>) emission in the reaction of O<sub>3</sub> with ethylene, propene, 3-methyl-1-butene, and 1,3-butadiene.<sup>57,58</sup> The effect was rationalized by assuming that the O<sub>2</sub> scavenges a radical which would otherwise react with an intermediate needed for the formation of CH<sub>2</sub>O. The exact reason for the enhancement is, however, unknown. More often O<sub>2</sub> will quench an emission by removing a needed atom or radical. For example, Meinel bands result from H + O<sub>3</sub> → OH(<sup>2</sup>Π<sub>i</sub>) + O<sub>2</sub>, and are quenched in the presence of sufficient O<sub>2</sub> because of H + O<sub>2</sub> + M → HO<sub>2</sub> + M.<sup>58</sup>

O<sub>2</sub> was found to quench both singlet<sup>64</sup> and triplet<sup>60</sup> CF<sub>2</sub> emission in the reaction of O<sub>3</sub> with C<sub>2</sub>F<sub>4</sub>. This is a surprising result since singlet CF<sub>2</sub> would not be expected to be rapidly quenched by O<sub>2</sub>. The explanation offered was first postulated in work with O atoms and C<sub>2</sub>F<sub>4</sub>,<sup>65</sup> a mechanism involving triplet-triplet annihilation:

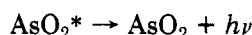
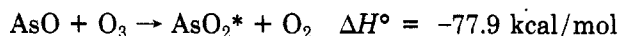
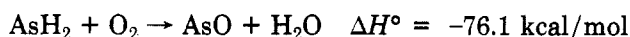
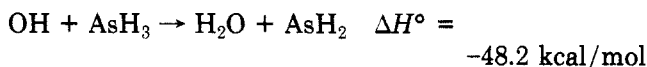
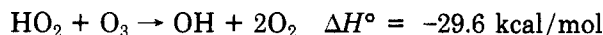
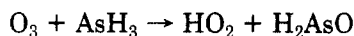


The addition of O<sub>2</sub> removes triplets (and therefore singlets) via the reaction CF<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) + O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) → CF<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) + O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and this was indicated by a large increase in the peak at 762 nm from the O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup> → <sup>3</sup>Σ<sub>g</sub><sup>-</sup>) transition.<sup>60,65</sup> This effect is shown in Figure 2.

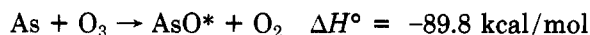
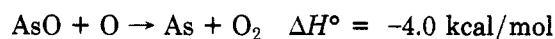
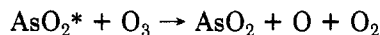
**Group 5 Oxide Kinetics.** The emission from NO/O<sub>3</sub> reaction enables the rate to be measured very accurately. Schurath and co-workers found no Arrhenius curvature in the range 283–443 K<sup>66</sup> but that the activation energy of the chemiluminescent pathway depended on the wavelength used for detection.<sup>67</sup> Borders and Birks<sup>68</sup> observed Arrhenius curvature in the range 200–350 K and gave the rate constant as 8.9 × 10<sup>-19</sup> T<sup>2.2</sup>e<sup>-1520/RT</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This reaction has been further studied by beam techniques which showed the effect of orientation of the NO molecule in the reactive collision,<sup>69</sup> and also in a magnetic field to determine if the fine structure state of the NO (<sup>2</sup>Π<sub>1/2</sub>)

and  ${}^2\Pi_{3/2}$ ) affected the CL.<sup>70</sup> Focusing the magnetic field did cause a small increase in chemiluminescence.

The reactions of ozone with phosphine, arsine, and stibine are very complex. Fraser and Stedman<sup>49</sup> found that the  $\text{AsH}_3/\text{O}_3$  system had an induction period and then gave a discrete emission in the ultraviolet region and a continuum in the visible, shown in Figure 1 with the spectral assignments in Table I. A 24-step mechanism was needed for the computer simulation and a possible pathway for the visible emission is



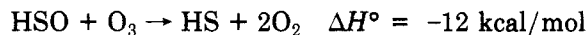
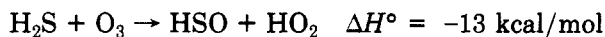
The ultraviolet emission was postulated to come from the foregoing steps and



It may be added parenthetically that the reaction between nickel carbonyl and ozone is probably just as complex with the emission from excited nickel oxide arising from the reaction  $\text{Ni} + \text{O}_3 \rightarrow \text{NiO}^* + \text{O}_2$ .<sup>42</sup>

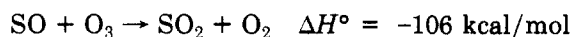
**Formation of HSO and  $\text{SO}_2$ .** The  $\text{HSO}^*$  and  $\text{SO}_2$  emissions from the reactions of ozone with  $\text{H}_2\text{S}$  and mercaptans have already been considered. Although much is known about the emitters,<sup>53,55a</sup> the reaction mechanism leading to them is not well understood.

The reaction producing  $\text{HSO}^*$  is probably  $\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$ . The exothermicity of this reaction is around 65 kcal/mol, the uncertainty being due mostly to lack of an accurate value for  $\Delta H_f^\circ(\text{HSO})$ . However, the pathway leading to the formation of HS is unclear. The reaction  $\text{H}_2\text{S} + \text{O}_3 \rightarrow \text{HS} + \text{HO} + \text{O}_2$  has  $\Delta H^\circ = 15 \text{ kcal/mol}$  although a possible alternative is the sequence:



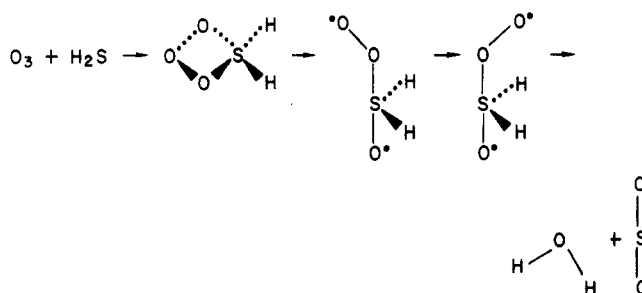
The heats of reaction are obtained by taking  $\Delta H_f^\circ(\text{HSO}) \approx 13 \text{ kcal/mol}$ ,<sup>55a</sup> other values having much less uncertainty.<sup>71</sup> In the case of the reaction of  $\text{O}_3$  with methyl mercaptan and dimethyl sulfide, no HSO bands were seen presumably because HS was not formed.<sup>51</sup>

The formation of electronically excited  $\text{SO}_2$  from the reaction of  $\text{O}_3$  with sulfides has been assumed to follow sequences such as  $\text{CH}_3\text{SH} + \text{O}_3 \rightarrow \text{CH}_3\text{O}_2 + \text{HSO}$  and  $\text{HSO} + \text{O}_3 \rightarrow \text{HO} + \text{SO} + \text{O}_2$  followed by



The bimolecular reaction  $\text{O}_3 + \text{H}_2\text{S} \rightarrow \text{SO}_2 + \text{H}_2\text{O}$  ( $\Delta H^\circ = -158.1 \text{ kcal/mol}$ ) was discounted because it is at variance with the observed kinetics<sup>72</sup> and would require a very complicated molecular rearrangement.

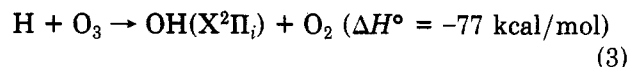
Glinski, Sedarski, and Dixon<sup>73</sup> have obtained evidence for the single-collision reaction of  $\text{O}_3$  with  $\text{H}_2\text{S}$  to produce electronically excited  $\text{SO}_2$ . The considerable rearrangement needed was postulated as



How important this concerted reaction is in the overall reaction between  $\text{O}_3$  and  $\text{H}_2\text{S}$  (or other sulfides) is an interesting and unresolved question.

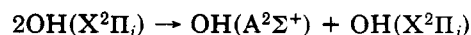
**Sources of  $\text{O}_3$ /Alkene Emission.** There is a huge literature on the ozonization of organic compounds<sup>12</sup> with much recent work on the structure and decomposition of ozonides.<sup>74</sup> Even the reaction of ozone with a molecule as simple as ethylene has extremely complex kinetics<sup>57,75-77</sup> with many reaction channels imperfectly understood. We shall indicate here possible sources for most of the emitters listed in Table II.

$\text{OH}(\text{X}^2\Pi, \nu \leq 9)$  emission probably occurs whenever  $\text{O}_3$  reacts with hydrogen-containing compounds. This vibrational-rotational emission has been shown to be identical with the Meinel band emission from

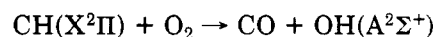


and is therefore a strong indication of the presence of H atoms.<sup>57</sup> These H atoms probably arise from the decomposition of the Criegee intermediate and Herron and Huie<sup>75</sup> have estimated that in the  $\text{O}_3/\text{C}_2\text{H}_4$  system about 9% of this intermediate decomposes to give H atoms via  $\text{H}_2\text{COO} \rightarrow 2\text{H} + \text{CO}_2$ . However, other sources have been suggested.<sup>58</sup> There have been indications that  $\text{H} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}$  may be a significant channel in the reaction of H atoms with ozone,<sup>78,79</sup> but current evidence is against this possibility.<sup>80</sup> Molecular oxygen is a relatively weak quencher for the Meinel bands.

$\text{OH}(\text{A}^2\Sigma^+)$  emission is almost as common as Meinel bands in  $\text{O}_3$ /alkene systems, as Table II shows. However, the source of this species cannot be from eq 3 because this reaction does not provide the 93.3 kcal/mol excitation energy needed for  $\text{OH}(\text{A}^2\Sigma^+, \nu' = 0)$ . Electronically excited OH can arise from vibrationally excited OH via energy pooling:<sup>81</sup>



This process, however, produces rotationally hotter  $\text{OH}(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi)$  emission than seen in  $\text{O}_3$ /alkene systems and in addition would not give the first-order dependence on  $\text{OH}(\text{X}^2\Pi_i)$  that has been observed by Finlayson, Pitts, and Atkinson.<sup>57</sup> In the case of  $\text{O}/\text{C}_2\text{H}_4$  flames, reactions involving O atoms have been suggested<sup>82</sup> as precursors to  $\text{OH}(\text{A}^2\Sigma^+)$  but this seems less likely in  $\text{O}_3$ /alkene systems. A more likely possibility<sup>83</sup> is the reaction



which would provide 159 kcal/mol. However, the

TABLE III.<sup>a</sup> Primary Pathways for Reactions of Ozone with Ethylenes

reaction	identified emitters	ref	$\Delta H^\circ$ , kcal/mol
$O_3 + C_2H_4 \xrightarrow{1} HCHO + HCOOH$	HCHO*	57, 58	-163
$O_3 + C_2H_3F \xrightarrow{2a} HCOF + HCOOH$			-183
$\xrightarrow{2b} HCHO + FCO + OH$			-60
$\xrightarrow{2c} HCHO + CHF + O_2$			+11
$O_3 + 1,1-C_2H_2F_2 \xrightarrow{3a} COF_2 + HCOOH$			-199
$\xrightarrow{3b} HCHO + CF_2 + O_2$			-27
$O_3 + 1,2-C_2H_2F_2 \xrightarrow{4a} HCOF + FCO + OH$	FCO*	58, 64, 87	-78
$\xrightarrow{4a} HCOF + CHF + O_2$			-8
$O_3 + C_2HF_3 \xrightarrow{5a} COF_2 + FCO + OH$	FCO*	87	-104
$\xrightarrow{5b} COF_2 + CFH + O_2$			-33
$\xrightarrow{5c} HCOF + CF_2 + O_2$	CF <sub>2</sub> *		-55
$O_3 + C_2ClF_3 \xrightarrow{6a} COF_2 + FCO + ClO$	FCO*	87	-76
$\xrightarrow{6b} COF_2 + CClF + O_2$			-52
$\xrightarrow{6c} COClF + CF_2 + O_2$			-54
$O_3 + C_2F_4 \xrightarrow{7} COF_2 + CF_2 + O_2$	CF <sub>2</sub> *	64	-73

<sup>a</sup> Reprinted with permission from ref 61. Copyright 1981, American Chemical Society.

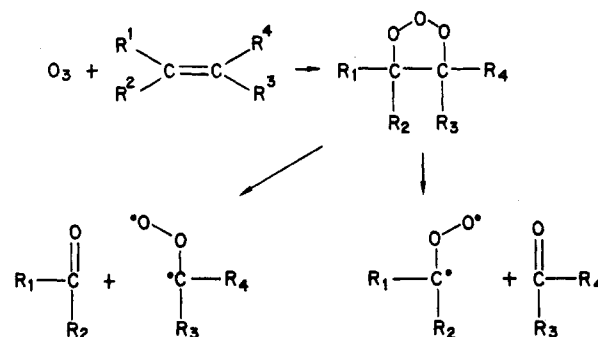
source of CH is not at all clear, although CH(<sup>2</sup>Δ) emission appears from several substrates in Table II and it is a common constituent of combustion bands. Molecular O<sub>2</sub> often quenches OH(A<sup>2</sup>Σ<sup>+</sup>) emission.<sup>57</sup>

CH(<sup>2</sup>Δ → <sup>2</sup>Π) emission has been observed in the reaction of O<sub>3</sub> with acetylene, allene, and aromatics and as previously mentioned, the 431-nm peak is commonly seen in combustion and is not appreciably quenched by O<sub>2</sub>. The reaction pathway leading to the formation of CH is still uncertain.

CH<sub>2</sub>O(<sup>1</sup>A<sub>2</sub>) emission has been seen in most of alkene systems listed in Table II. The fact that both terminal and internal alkenes yield formaldehyde emission is taken as evidence for at least two mechanisms for the formation of CH<sub>2</sub>O(<sup>1</sup>A<sub>2</sub>).<sup>57</sup> The possibilities include α-H and β-H abstraction from the ozonide intermediate prior to the rupture of the five-membered ring, and the reaction of O<sub>3</sub> with methylene peroxide: CH<sub>2</sub>O<sub>2</sub> + O<sub>3</sub> → CH<sub>2</sub>O + 2O<sub>2</sub>. The latter reaction has ΔH<sup>o</sup> = -110 kcal/mol compared to 80.5 kcal/mol which is the excitation energy for CH<sub>2</sub>O(<sup>1</sup>A<sub>2</sub>). Formaldehyde emission is usually not quenched by O<sub>2</sub>.

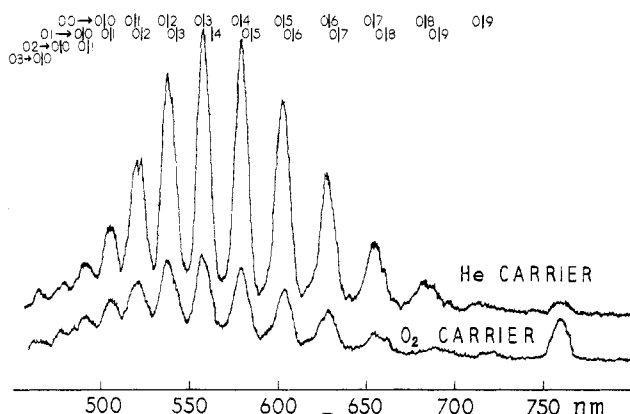
α-Diketones are formed in the triplet state in many of the systems under consideration and α-diketone phosphorescence is common in O<sub>3</sub>/alkene systems except for the halogenated alkenes. The species identified are glyoxal and methylglyoxal and Schurath, Gusten, and Penzhorn have concluded that biacetyl does not contribute to O<sub>3</sub>/alkene CL.<sup>59</sup> They ruled out O<sub>2</sub> as a necessary precursor for α-diketone emission and gave a general rule for the formation of the emitter. Glyoxal phosphorescence is observed when one or two carbon atoms of the alkene double bond have an H atom and an alkyl group. Methylglyoxal phosphorescence occurs when one carbon atom on the double bond bears two methyl groups.

CF<sub>2</sub>(<sup>1</sup>B<sub>1</sub>, <sup>3</sup>B<sub>1</sub>) and CFO emissions occur in the reactions of O<sub>3</sub> with several fluoroethenes as shown in Table II. The Criegee mechanism for ozonolysis in the liquid phase is also valid in the gas phase<sup>84</sup> although biradicals rather than zwitterions are presumably formed.<sup>85</sup> We may also ignore secondary ozonides which are formed in the liquid phase.<sup>86</sup> The replacement of H atoms by halogen atoms reduces the number of possible products formed when the ozonide ring ruptures



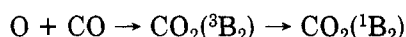
If secondary reactions, such as the decomposition of excited formic acid<sup>75</sup> are omitted, the reaction pathways for the ozonolysis of fluoroethenes may be listed with their corresponding reaction enthalpies<sup>61,87</sup> as shown in Table III. Where there is more than one pathway for the decomposition of a peroxy radical, the luminescence accompanies the more exothermic channel.

**The Ozone/Carbon Monoxide System.** Early work was done in the presence of O<sub>2</sub> at temperatures up to 200 °C and under these quasi-combustion conditions, CO flame bands were seen.<sup>88</sup> More recently, a visible emission was noted even at room temperature<sup>89</sup> and this emission was found to be oscillatory in a flow system.<sup>90</sup> Commercial CO contains carbonyls as im-



**Figure 2.** Visible/IR emission from the reaction  $O_3 + C_2F_4$  with He and  $O_2$  carriers: total pressure = 45 Torr, spectral slit width = 3 nm, uncorrected for photomultiplier response. Assignments are by Koda.<sup>65</sup> Reprinted with permission from ref 60. Copyright 1980, American Chemical Society.

purities<sup>42</sup> and when the impurity level was reduced the chain component of the reaction was correspondingly reduced.<sup>91</sup> The reaction is thus that between CO and O atoms produced by the thermal decomposition of  $O_3$ . Subsequent work<sup>92</sup> with added gases showed that the kinetics of the emitted light was in conformity with two sources of  $CO_2(^1B_2)$ . These are



and



This may help explain some of the discordance in the literature on the reaction between CO and O atoms.<sup>93</sup>

Registry No.  $O_3$ , 10028-15-6.

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