STRUCTURAL EFFECTS ON THE CHEMILUMINESCENCE FROM THE REACTION OF OZONE WITH SELECTED ORGANIC COMPOUNDS

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Summary

In order to test experimentally the reaction pathways postulated from previous experimental and theoretical investigations, the following studies were carried out.

(1) An investigation into the effect of pressure and O_2 on the OH Meinel band emission from the reaction of O_3 with simple olefins.

(2) An extension of previous studies of chemiluminescence from low pressure gas phase ozone reactions to the following classes of compounds: cyclic olefins (cyclopentene), alkynes (acetylene), diolefins (allene, 1,3-butadiene) and unsaturated aldehydes (acrolein and crotonaldehyde). These compounds provide possibilities for diversion of the normal reaction paths not present in simple olefins.

(3) In order to test the mechanisms proposed in the literature to account for chemiluminescent species studies were carried out on the following selected organic compounds to determine whether the chemiluminescence observed was predicted by the mechanistic theories: 3-methyl-1-butene to attempt to determine the mechanistic pathway for the production of glyoxal phosphorescence; 1,1- and 1,2-difluoroethylene, 3,3,3-trifluoropropylene, 1,1-dichloropropylene, cyclopentene, acrolein, *trans*-3-hexene and *trans*-4-octene to investigate the pathways for production of formaldehyde fluorescence; a series of deuterated and partially deuterated propylenes for the production of OH Meinel band emission.

The data and chemiluminescent spectra obtained are reported, leading to the conclusion that the present theories of ozone—olefin reactions do not entirely predict the chemiluminescing species observed. Furthermore, it appears that the overall mechanism for production of vibrationally excited hydroxyl radicals from ozone—olefin reactions is so complex that a satisfactory mechanism cannot easily be deduced by simply studying the effect of variable reactant concentrations and total pressure.

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Introduction

Studies of the gas phase reactions of ozone with simple olefins date from the early investigations of Briner [1, 2] in which some of the products were identified. These reactions have come under increasing scrutiny since Haagen-Smit [3] first demonstrated the phytotoxicant properties of ozone–olefin reaction products and awareness grew of the role these reactions play in the production of photochemical smog [4]. Thus, numerous studies of products [5 - 22], reaction kinetics [7, 8, 11 - 14, 16, 17, 20, 23 - 35] and chemiluminescence [16, 17, 36 - 49] of the gas phase reactions of ozone with simple olefins and alkynes have been performed together with theoretical examinations [34, 50 - 52] of the thermochemistry and stability of proposed reaction intermediates. In our laboratories investigations of the chemiluminescence accompanying these reactions have constituted a significant portion of our overall efforts to understand better the underlying mechanisms involved.

Chemiluminescence from $CH_2O(^1A'')$ and $OH(X^2\Pi)_{v \leqslant 9}$ was observed from the ozonolysis of ethylene, propylene, 1-butene, isobutene, *cis-* and *trans-*2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene, while emission from $OH(A^2\Sigma^+)$ was observed from ethylene, isobutene and *cis-*2-butene [17]. The vibration–rotation emission from $OH(X^2\Pi)_{v \leqslant 9}$ was identical to the OH Meinel band emission from the reaction

$$H + O_3 \rightarrow OH(X^2\Pi)_{v \leqslant 9} + O_2$$
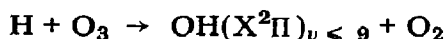
which strongly suggests that H atoms are formed in low pressure ozone–olefin reactions. The production of H atoms was explained by rearrangement of the Criegee biradical to give excited carboxylic acids with sufficient energy to decompose yielding H atoms [53]. However, alternative paths for H atom production which are also thermochemically reasonable can be suggested. For example, formyl radicals which are formed in ozone–olefin reactions [15] may generate H atoms by the following sequence:

$$O_3 + CHO \rightarrow HCO_2^* + O_2 \qquad \Delta H^\circ \approx -75 \text{ kcal mol}^{-1}$$

$$HCO_2^* \rightarrow H + CO_2$$
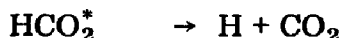
In the presence of O_2 glyoxal phosphorescence was identified [17] in the reactions of ozone with *cis-* or *trans-*2-butene, and methylglyoxal phosphorescence was detected in reactions with isobutene, 2-methyl-2-butene and 2,3-dimethyl-2-butene. The O'Neal and Blumstein mechanism [50] does not predict dicarbonyl phosphorescence. Modification of the mechanism (path h in Fig. 1) provided a plausible explanation of the experimental observations [17].

The number of quanta emitted per molecule of reactant consumed at 4.6 Torr total pressure in the ethylene and *cis-*2-butene reactions was estimated [17] to be 10^{-7} for $CH_2O(^1A'' \rightarrow {}^1A_1)$ and 10^{-5} for $(CHO)_2(^3A_u \rightarrow {}^1A_g)$ in the *cis-*2-butene reaction. Approximately 10^{-7} quanta were emitted in the (9, 3) transition of vibrationally excited OH per molecule of reactant
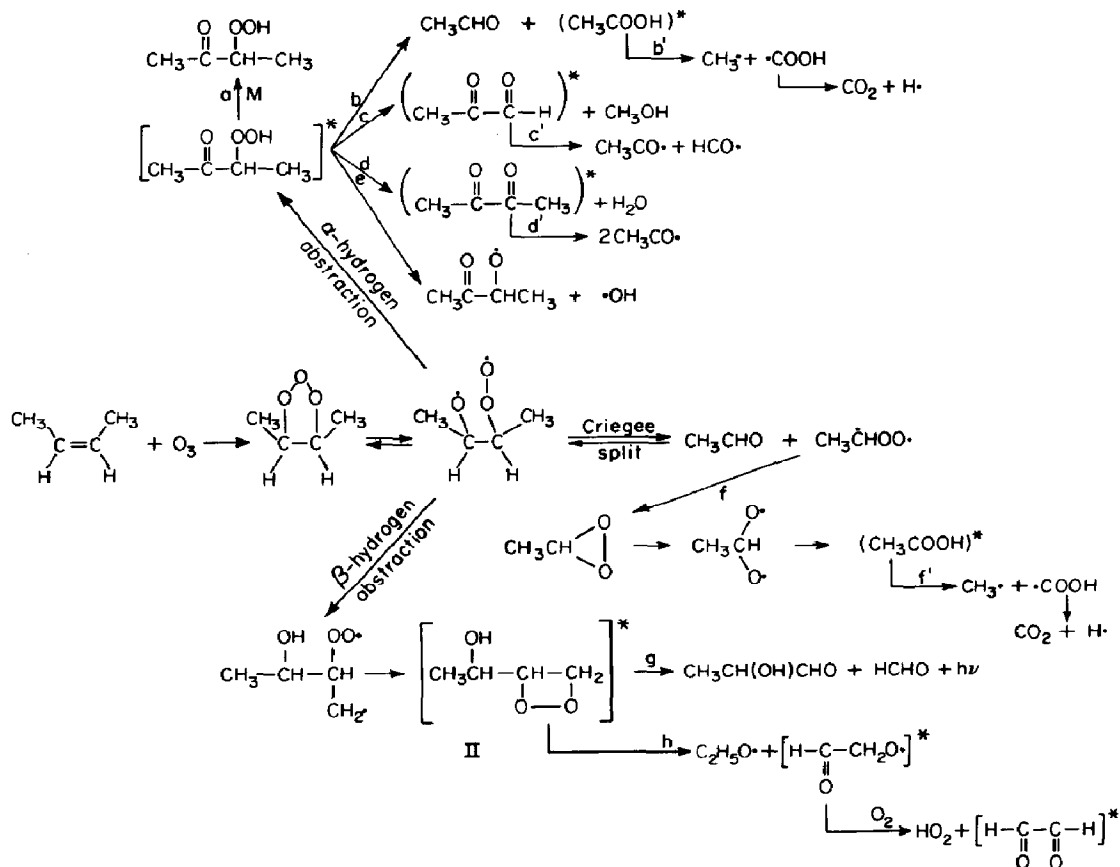
Fig. 1. Mechanism for the gas phase reaction of ozone with 2-butene as proposed in refs. 50 and 17.

consumed, which, when combined with the data of Garvin *et al.* [54] in order to estimate the total emission intensity based on that of the (9, 3) transition, indicates that the formation of vibrationally excited OH is an efficient process under the conditions used.

In the ethylene, *cis*-2-butene and isobutene reactions the decay of the light emission from each excited species was exponential with time when the diluent gas was O_2, but non-exponential when the diluent was N_2 or He [17]. Rate constants, determined from the loss of O_3 in both O_2 and N_2 diluents, were a factor of 2 - 5 times greater in N_2, assuming a 1:1 stoichiometry [17]. In 10 Torr O_2 the measured rate constants [17] for the ethylene, *cis*-2-butene and isobutene reactions were in general agreement with literature values [16, 27 - 30, 34, 35].

Major products of the reactions of *cis*-2-butene with ozone in either O_2 or N_2 diluent were acetaldehyde and 2-butanone [17]. The latter compound was proposed to result from the reactions of OH with *cis*-2-butene [17]. Methylvinylketone was observed only in O_2 and was suggested to be formed following attack of O_2 upon the $CH_2=CHCHCH_3$ radical.

In a photoionization mass spectrometric study of the reaction of ozone with *cis*-2-butene [15] a mass peak corresponding to the ozone–olefin adduct

(m/e = 104) was observed to increase linearly with time. This ion was tentatively identified as the α-ketohydroperoxide subsequently predicted (path a in Fig. 1) by the O'Neal and Blumstein mechanism [50]. An adduct ion was also observed in a field desorption mass spectrometric study of the reaction of ozone with 1-butene [21]. Recently Niki and coworkers [22] have studied the reaction of O_3 with a variety of olefins using Fourier interferometric spectroscopy. In addition to the previously observed products, such as aldehydes, ketones, acids, alcohols and alkanes, they observed infrared absorption bands, shown to be those of secondary ozonides, with yields of about 10 - 15% [22].

In order to test the postulated reaction pathways leading to chemiluminescent species, the following studies were carried out.

(1) An investigation was made into the effect of pressure and O_2 on the OH Meinel band emission from the reaction of O_3 with the simple olefins.

(2) An extension was made of our studies of chemiluminescence from low pressure gas phase ozone reactions to the following classes of compounds: cyclic olefins (cyclopentene), alkynes (acetylene), diolefins (allene, 1,3-butadiene) and unsaturated aldehydes (acrolein and crotonaldehyde). These compounds provide possibilities for diversion of the normal reaction paths not present in simple olefins.

(3) In order to test the mechanism proposed [17, 50] to account for chemiluminescent species, studies were carried out on selected organic compounds to determine whether the chemiluminescence observed was predicted by the mechanistic theories. The results of these studies are reported here, and lead to the conclusion that the present theories of ozone–olefin reactions do not entirely predict the chemiluminescing species observed.

Experimental

A stopped-flow reactor was constructed specifically to provide a constant viewing geometry to follow slow chemiluminescent decays and also to act as a stirred-flow reactor to obtain chemiluminescent spectra. A schematic diagram of this apparatus is shown in Fig. 2.

An externally silvered cylindrical Pyrex flow cell of 10 cm length and approximately 100 cm³ volume was used in this study. Emission was viewed end-on through a Pyrex window with a front aluminized mirror placed against the opposite window. Thus emission at wavelengths shorter than about 300 nm was not detectable. Reactants and diluent gases were passed at atmospheric pressure through a calibrated flowmeter and needle valve and then into the low pressure flow stream. The reactants were premixed in a 50 cm³ Pyrex bulb before entering the chemiluminescence cell. Once the appropriate flows had been established and the emission intensity had stabilized, the stainless steel toggle valves isolating the viewing cell were simulta-
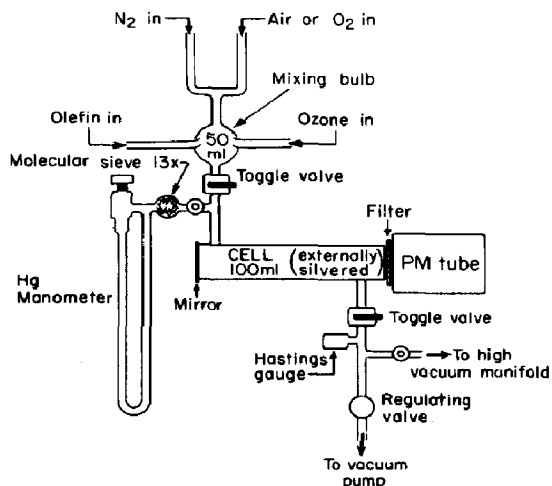
Fig. 2. Chemiluminescence detection system.

neously closed. The resulting emission decay was monitored by the detection system and recorded on a fast strip chart recorder equipped with an integrator. Flow rates were adjusted to ensure that the mean residence times in the mixing bulb and cell were short relative to the half-life of the ozone–olefin reaction being studied. Ozone concentrations were chosen to be 5 - 1000 times that of the organic concentration so that the O_3 concentration remained essentially constant during a run. The integrated emission intensity was related to the total chemiluminescence resulting from essentially complete consumption of the organic compound.

Chemiluminescence spectra were recorded using a 0.3 m McPherson spectrometer (600 grooves mm^{-1} grating, blazed at 500.0 nm) together with a cooled EMI 96590B photomultiplier (extended S-20 spectral response) whose output was fed to an SSR Model 1120 amplifier/discriminator and thence to an SSR Model 1105 data converter console.

Oxygen, purified by passage through traps containing Drierite and Linde molecular sieve 4A at 195 K, was passed through a Welsbach Model T-408 ozonizer to obtain O_3 in O_2. Ozone in nitrogen was obtained by diverting the O_3/O_2 stream through a silica gel trap at 195 K, pumping off the oxygen after an appropriate amount of ozone had been collected and then eluting the ozone from the silica gel with nitrogen which had been passed through a molecular sieve 4A trap at 195 K. Ozone concentration was continuously monitored by the calibrated 253.7 nm absorption of the ozone passing through a bypass section of square cross section quartz tubing.

Reactant flows were measured using calibrated rotameters. Total pressure in the reaction cell was measured using a mercury manometer which could be isolated from the cell during a run by a greaseless stopcock. All reactants were $\geqslant$ 98% purity as analyzed by gas chromatography.
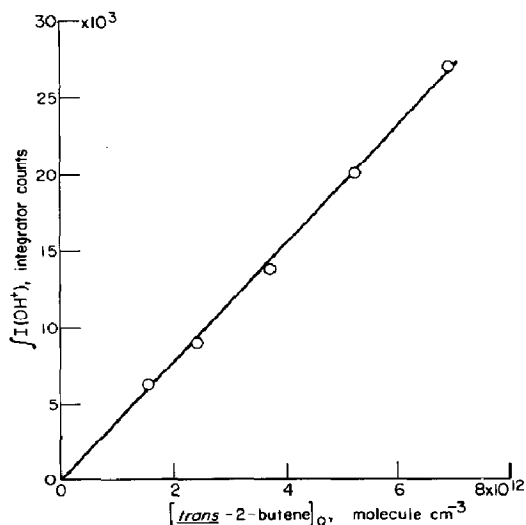
Results and discussion

Pressure dependence of OH Meinel band emission

A systematic study of the total OH emission intensity in the wavelength region $665 < \lambda < 850$ nm from the reaction of ozone with ethylene, propylene and *trans*-2-butene using O_2/N_2 mixtures as the diluent gas was carried out in which the following experimental parameters were varied: (i) total pressure, from 10 to 650 Torr, (ii) olefin concentrations, and (iii) O_2/N_2 or O_3/O_2 ratio at constant total pressure. By observing the effect of these variations upon the integrated emission intensity proposed mechanistic schemes for $OH(X^2\Pi)_{v \leqslant 9}$ production could be tested.

The treatment of Finlayson *et al.* [17] illustrates this approach:

$$O_3 + \text{olefin} \rightarrow \beta H + \text{other products} \tag{1}$$

where β, which may be a function of pressure, is the stoichiometric yield of H atoms produced per molecule of reacted olefin,

$$H + \text{olefin} \rightarrow \text{disappearance of H} \tag{2}$$

$$H + O_3 \rightarrow OH^\dagger + O_2 \tag{3}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{4}$$

$$OH^\dagger + \text{olefin} \rightarrow \text{disappearance of } OH^\dagger \tag{5}$$

$$
OH^\dagger + O_3 \left\{
\begin{array}{ll}
\rightarrow HO_2 + O_2 & \text{(6a)} \\
\rightarrow H + O_2 + O_2 & \text{(6b)} \\
\rightarrow OH + O + O_2 & \text{(6c)}
\end{array}
\right.
$$

$$OH^\dagger \rightarrow OH + h\nu \tag{7}$$

where $OH^\dagger$ refers to $OH(X^2\Pi)_{v \leqslant 9}$. Flow studies [55] have shown that reaction (6b) may be neglected. With ozone in excess, $k_2[\text{olefin}] \ll k_3[O_3]$, $k_5[\text{olefin}] < k_6[O_3]$, and $k_7 \ll k_6[O_3]$. If reactions (2) and (5) are neglected and the steady state approximation is applied to all radical species, the following expression is obtained for the OH emission intensity at any time t after the flow is stopped:

$$I(OH^\dagger) = \frac{\alpha\beta k_1 k_3 k_7 [O_3]^2 [\text{olefin}]_t}{k_6[O_3]\,(k_3[O_3] + k_4[O_2]\,[M])} \tag{I}$$

where α is the detection efficiency of the detector.

Making the reasonable assumption that $-d[\text{olefin}]/dt = k_1[O_3][\text{olefin}]_t$ and integrating from $t = 0$ to $t = \infty$ yields an expression for the total integrated emission intensity I_T:

$$I_T = \int_{t=0}^{t=\infty} I(OH^\dagger) = \frac{\alpha\beta k_3 k_7 [\text{olefin}]_0 [O_3]}{k_6[O_3]\,(k_3[O_3] + k_4[O_2][M])} \tag{II}$$

Fig. 3. Plot of $\int I(OH^\dagger)$ against *trans*-2-butene concentration: P_{O_3}, 0.17 Torr; P_{O_2}, 4.5 Torr; P_{total}, 18 Torr.
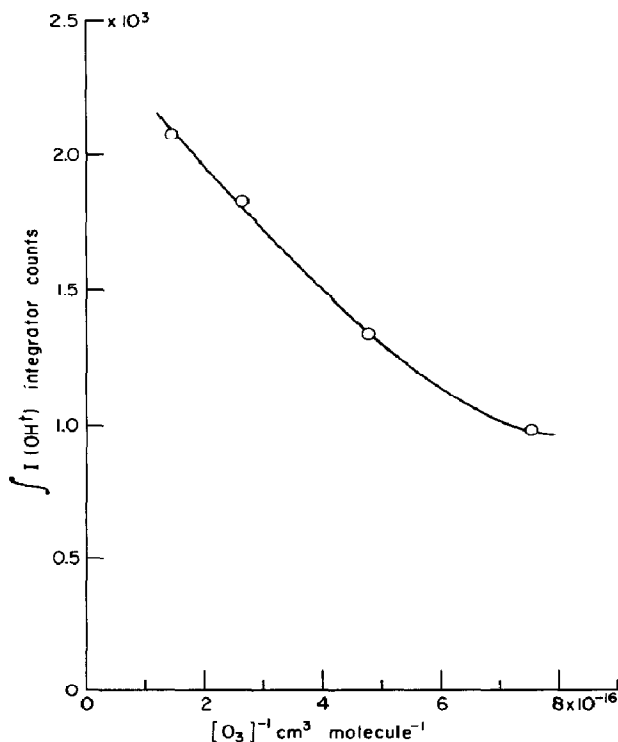
Fig. 4. Plot of $\int I(OH^\dagger)$ against $[O_3]^{-1}$ for *trans*-2-butene: $P_{trans\text{-2-butene}}$, 8.4 $\times$ 10^{-5} Torr; P_{O_2}, 13.2 Torr; P_{total}, 13.2 Torr.

where [olefin]$_0$ is the initial olefin concentration. Thus, I_T should be proportional to initial olefin concentration, as is observed (Fig. 3). At low total pressures $k_3[O_3] \gg k_4[O_2]$ [M] and therefore I_T should be proportional to $[O_3]^{-1}$. Figure 4 shows that this is not the case, although the curvature is most pronounced at lower ozone concentration where the previous assumptions may not rigorously hold. Rearranging eqn. (II) yields

$$I_T^{-1} = \frac{k_6[O_3]}{\alpha\beta k_7[\text{olefin}]_0} + \frac{k_4 k_6[O_2][M]}{\alpha\beta k_3 k_7[\text{olefin}]_0} \tag{III}$$

At constant $[O_3]$, [olefin]$_0$ and total pressure a plot of I_T^{-1} against $[O_2]$ should yield a straight line of slope $k_4 k_6[M]/\alpha\beta k_3 k_7[\text{olefin}]_0$ and intercept $k_6[O_3]/\alpha\beta k_7[\text{olefin}]_0$. Figure 5 is a plot of I_T^{-1} *versus* $[O_2]$ at constant propylene and ozone concentrations and at a total pressure of 650 Torr. The curvature of the plot is not consistent with the postulated mechanism for $OH^\dagger$ production as predicted by eqn. (III).

Several additional mechanisms were formulated which involved pressure quenching of $OH^\dagger$, additional participation of ozone in H atom production (*i.e.* reactions of ozone with possible intermediate species) and additional reactions of ozone and oxygen with intermediates. None of these mechanisms
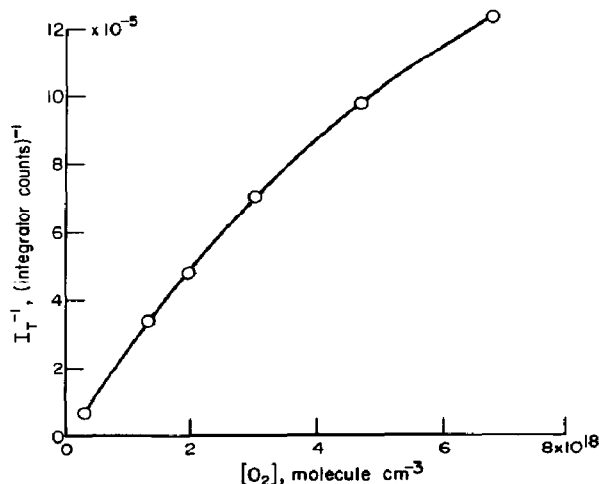
Fig. 5. Plot of I_T^{-1} against O_2 concentration for propylene: $P_{\text{propylene}}$, 0.21 Torr; P_{O_3}, 0.38 Torr; P_{total}, 650 Torr.

fitted the experimental data. It appears that the overall mechanism for production of vibrationally excited hydroxyl radicals from ozone–olefin reactions, and hence the H atom production efficiency, is so complex that a satisfactory mechanistic scheme cannot readily be deduced solely by studying the effect of variable reactant concentrations and total pressure upon the integrated OH† emission intensity.

The pressure dependence of the Meinel band emission from the reactions of ozone with ethylene, propylene and *trans*-2-butene may be summarized as follows. For all three olefins the integrated emission intensity at constant oxygen, ozone and olefin concentrations (ozone in excess of olefin) and a total oxygen pressure of about 10 Torr was reduced by a factor of 10 when the total pressure was increased to 650 Torr by addition of N_2. However, for the same olefins, when air was used as diluent gas rather than N_2, the intensity at 650 Torr was reduced relative to the 10 Torr values by factors of 97, 164 and 244, respectively. When the integrated OH† intensities were corrected for the contribution of reaction (4), a dependence upon oxygen concentration remained. Since O_2 and N_2 have nearly equal cross sections for quenching of vibrationally excited OH [56], this excess dependence must be attributed to interception of intermediates (which otherwise would react to yield H atoms) by O_2 rather than to a greater OH† quenching efficiency attributable to O_2. In addition, the relative efficiency of O_2 scavenging of radical intermediates seemed to increase with increasing size of the intermediates.

Chemiluminescent emission from the reaction of O_3 with acetylene, allene, 1,3-butadiene and crotonaldehyde

These compounds were chosen to represent classes of organic compounds not previously studied.

Allene, acetylene-h_2 and acetylene-d_2

The chemiluminescent spectra from the reaction of O_3 with C_2H_2 and allene have been reported elsewhere [47], and hence only a brief summary is given here together with a description of the chemiluminescence from the reaction of O_3 with C_2D_2.

The spectra of the chemiluminescence from the reaction of ozone with acetylene-h_2 in about 7 Torr N_2 showed major emission features due to CHO $(C \rightarrow X^2A')$, $CH(^2\Delta \rightarrow ^2\Pi)$ and $OH(X^2\Pi)_{v<9}$ at low resolution. To identify more clearly the emitting species the spectra were run at higher resolution with reactant flows adjusted to maximize the emission intensity, and are shown in Fig. 6. The most prominent feature from C_2H_2 is the $CH(^2\Delta)$ emission at 431.3 nm. The B bands and the A_0 and A_1 vibrational progressions of HCO [57] are also clearly present. Possible other emissions are those of $OH(A^2\Sigma^+)$ near 315 nm, $CH(^2\Sigma^-)$ at 390.3 nm and $C_2(B^3\Pi_g, v' = 0 \rightarrow X^3\Pi_u, v'' = 6)$ at 328.2 nm. Several points concerning the chemiluminescence from the $O_3 + C_2D_2$ reaction, run under identical conditions to the $O_3 + C_2H_2$ reaction, are noteworthy (Fig. 6). The integrated DCO emission is 2.8 times as intense as the HCO emission from the $O_3 + C_2H_2$ reaction. The $CD(^2\Delta \rightarrow ^2\Pi)$ emission is only 0.44 times as intense as the $CH(^2\Delta \rightarrow ^2\Pi)$ emission and probably demonstrates a kinetic isotope effect operating at some step(s) in the formation process. The failure to observe C_2 emission is probably also due to a kinetic isotope effect as two C—D bonds must be broken to produce this species.
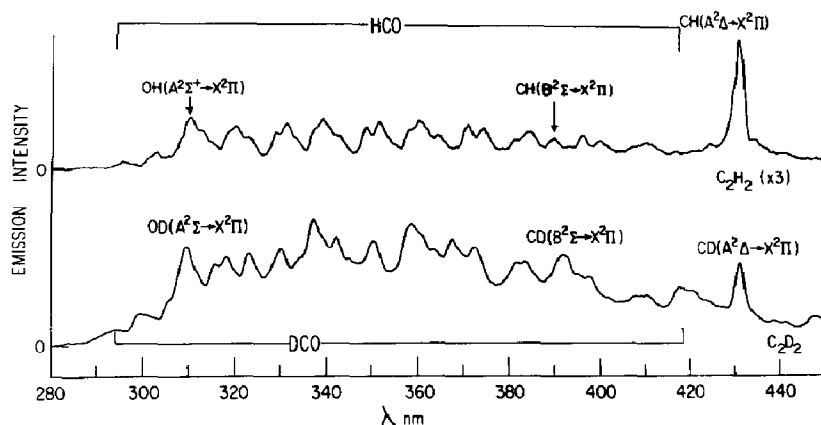

Fig. 6. Chemiluminescent emission ($280 < \lambda < 450$ nm) from the reactions of O_3 with C_2H_2 and C_2D_2. Total pressure 6.9 Torr N_2.

The chemiluminescence spectra (spectral bandpass, 5 nm) obtained from the reaction of ozone with allene are shown in Fig. 7, taken at total pressures of 6.5 and 41.5 Torr of N_2 respectively. At the lowest pressure prominent peaks attributable to $OH(A^2\Sigma^+)$, $CH(^2\Delta)$ and Meinel band emissions are apparent. The broad continuum extending from 330 to 550 nm and peaking near 430 nm is most probably due to formaldehyde emission. At 41.5 Torr the
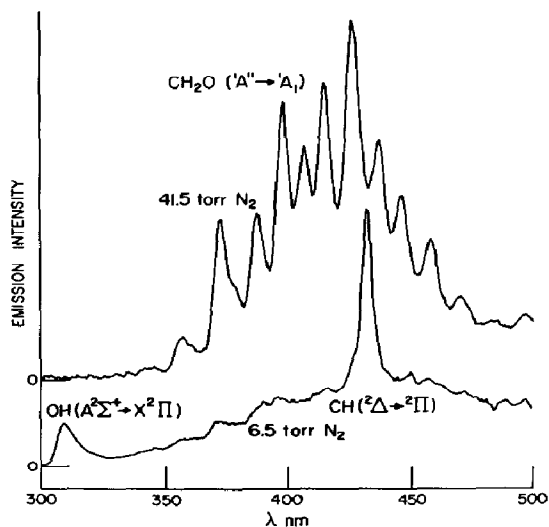
Fig. 7. Chemiluminescence from the reaction of O_3 with allene in N_2.

spectrum given in Fig. 7 shows the absence of $OH(A^2\Sigma^+)$ and $CH(^2\Delta)$ emission and greatly enhanced CH_2O intensity such that the vibrational structure is more readily discerned. Meinel band emission intensity (not shown) is generally reduced at the higher pressure.

When nitrogen was replaced with an equal amount of oxygen in the low pressure studies, all other conditions remaining the same, no chemiluminescence could be detected from the reaction of ozone with acetylene. Only formaldehyde emission was detectable from the ozone—allene reaction in O_2 and the integrated emission intensity was reduced an order of magnitude from that in N_2.

Although the reactions of O_3 with propylene and 1,3-butadiene are known to give electronically excited and vibrationally excited OH emissions, the low levels of these impurities in the allene are inconsistent with their contribution to the relative intensity of the emission observed in the present study. Furthermore, $CH(^2\Delta)$ emission has not been detected from the reactions of O_3 with 1,3-butadiene and propylene under any conditions so far employed.

My et al. [41] observed $OH(A^2\Sigma^+)$, $CH(B^2\Sigma^-$ and $^2\Delta)$ and $C_2(A^3\Pi_g)$ emissions in the ultraviolet and visible from the reaction of O_3 with acetylene, while Toby [46] observed a $CH_2O(^1A'')$ emission from O_3 with allene. The present observations are in agreement with these studies as discussed previously [47].

The similarity between the chemiluminescence spectra from this ozonolysis study and the spectra derived from other studies of acetylene oxidations is striking. Meinel band emissions have been identified from the reaction of oxygen atoms with acetylene [58]. In addition, all other emissions reported here have been observed [59] in C_2H_2–O_2 flames, in shock tube studies of C_2H_2–O_2–Ar mixtures and from O_2–C_2H_2 reactions. The fact that the ozone—

acetylene reaction gives chemiluminescence analogous to acetylene combustion reactions, whereas the reactions of ozone with simple olefins do not produce such a variety of emitting species, may be related to the relative enthalpies of formation of the respective hydrocarbons: ΔH_f° (C_2H_2) = 54 kcal mol^{-1}; ΔH_f° (olefins) $\leqslant$ 12.5 kcal mol^{-1}. Thus, the additional enthalpy released upon reaction of ozone with acetylene should make subsequent fragmentation reactions more probable. This would result in a concomitant increase in the radical concentrations which may approximate those present in combustion processes [60]. A similar argument would apply to the ozone–allene reaction (ΔH_f^0(allene) = 46 kcal mol^{-1}) where CH($^2\Delta$) production appears to be unique among ozone–olefin reactions.

1,3-Butadiene

The reaction of ozone with 1,3-butadiene yielded chemiluminescence characteristic of the simple mono-olefins. The OH($A^2\Sigma^+$) emission was identifiable near 312 nm in the spectrum taken at 6.3 Torr in N_2, while formaldehyde ($^1A''$) emission was confirmed by the spectrum taken at 39.8 Torr in O_2 (Fig. 8). Some emission in the region characteristic of ^3A_u α-dicarbonyls (about 522 nm) was also observed when O_2 had quenched the obscuring Meinel band from OH($X^2\Pi$)$_{v \leqslant 9}$.
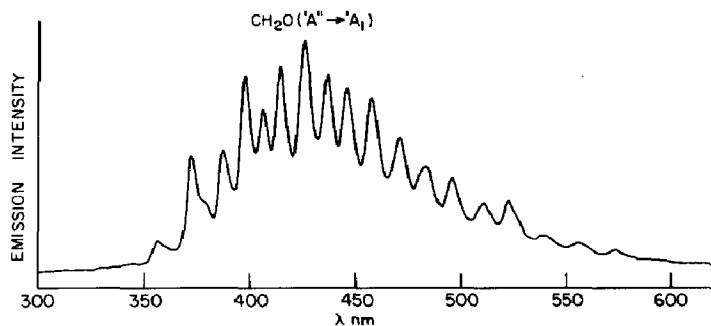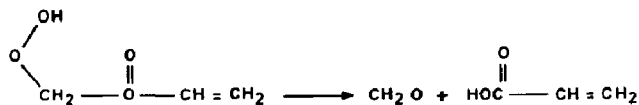

Fig. 8. Chemiluminescent spectrum from the reaction of O_3 with 1,3-butadiene in O_2 at a total pressure of 29.8 Torr.

Electronically excited formaldehyde production is not possible via the O'Neal–Blumstein [50] β-H abstraction route, outlined earlier, from the reaction of ozone with 1,3-butadiene. Even if the alkoxide radical was able to abstract the vinyl β-hydrogen atom in competition with other available reaction pathways, decomposition of the resulting dioxetene species would yield ketene, not formaldehyde. If the route to $H_2CO(^1A)$ is the same as that proposed for O_3 + C_2H_4 [17] and other terminal olefins [17] (see discussion of the ozone + deuterated propenes below) then the α-ketohydroperoxide precursor must possess more than 20 kcal mol^{-1} excess energy since the enthalpy of the decomposition

is only $- 60.4$ kcal mol^{-1} and the excitation energy of $H_2CO(^1A'')$ is 80.5 kcal mol^{-1} with respect to the ground state [61].

Another pathway for the production of formaldehyde emission from the reaction of ozone is that proposed by Wadt and Goddard [52]. Following cleavage of the initial molozonide the molecule may fragment into a carbonyl compound and methylene peroxide:

$$\underset{\substack{\\ CH_2 \text{---} CH \\ \quad\quad \backslash \\ \quad\quad CH = CH_2}}{\overset{\substack{O\cdot \\ / \\ O \quad \quad \cdot O \\ \backslash \quad\quad / }}{}} \quad \longrightarrow \quad \cdot CH_2 OO\cdot \; + \; \overset{O}{\overset{\parallel}{HC}} \text{---} CH = CH_2$$

Subsequent reaction of the methylene peroxide with ozone could yield electronically excited formaldehyde plus oxygen:

$$\cdot CH_2OO\cdot \; + \; O_3 \; \rightarrow \; CH_2O^* + 2O_2 \qquad \Delta H° = - 109.8 \text{ kcal mol}^{-1}$$

For this scheme to be operable the rate constant for reaction of methylene peroxide with ozone must be orders of magnitude greater than that with oxygen since no diminution of H_2CO emission intensity is observed when O_2 is substituted for N_2.

Of the two mechanisms considered here, the former seems less likely in view of the substantial H_2CO emission intensity observed at 40 Torr in O_2. According to O'Neal and Blumstein's estimate [50], α-H abstraction should proceed with a rate less than 10^9 s^{-1}. Since the collision frequency at 40 Torr is near 10^9 s^{-1}, it is doubtful that a substantial fraction of any α-ketohydroperoxide formed would retain enough excess energy to produce $H_2CO(^1A')$ upon decomposition.

The nature of the emitting α-dicarbonyl compound, whose presence is inferred from the 522 nm band, cannot be deduced from examination of the spectra because of the low resolution used. Schurath $et\ al.$ [49] also observed a weak chemiluminescence at 520 nm from this reaction, but again could not identify the emitter on account of the low resolution used. Acyl–acyl radical recombination would occur with very low probability in the presence of almost 40 Torr O_2 and can therefore be ruled out. In contrast, one of the decomposition modes of the α-ketohydroperoxide suggested by O'Neal and Blumstein [50]

$$\underset{\substack{\\ HC \text{---} CH \\ \quad\quad \backslash \\ \quad\quad CH = CH_2}}{\overset{\substack{HO \\ \backslash \\ O \quad\quad O \\ \parallel \quad\quad / }}{}} \quad \longrightarrow \quad H_2O \; + \; \overset{O}{\overset{\parallel}{HC}} \text{---} \overset{O}{\overset{\parallel}{C}} \text{---} CH=CH_2 \qquad \Delta H° \sim -52 \text{ kcal mol}^{-1}$$

leads to α-dicarbonyl formation. With only 3 kcal mol^{-1} excess excitation of the α-ketohydroperoxide this pathway could yield the triplet excited α-dicarbonyl (energy of excitation $\approx$ 55 kcal mol^{-1} by analogy to related compounds) [62]. In fact, owing to the triply conjugated nature of the 1,2-diketo-3-butene molecule, the necessary excitation energy may be reduced relative to doubly conjugated α-dicarbonyls ($e.g.$ glyoxal, methylglyoxal).

Crotonaldehyde

The reaction run in N_2 at 6.3 Torr (Fig. 9) showed the presence of moderate $OH(A^2\Sigma^+)$ emission, intense $OH(X^2\Pi)_{v \leq 9}$ emission, glyoxal (^3A_u) emission and moderate carbonyl emission, which was very diffuse, together with the presence of bands tentatively assigned to CO_2 (similar to ozone + acrolein, see later). All emissions were quenched in O_2 suggesting probable radical reaction pathways to these emissions.
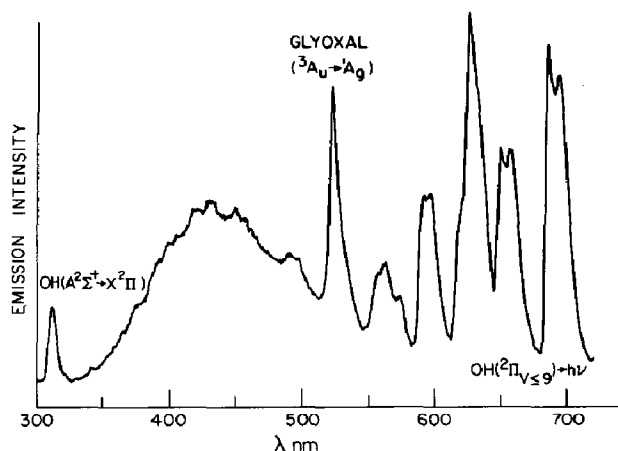

Fig. 9. Chemiluminescent spectrum from the reaction of O_3 and crotonaldehyde in N_2 at 6.3 Torr total pressure.

Tests of the recently proposed mechanisms [17, 50] for the production of chemiluminescence

(1) For cis-2-butene, Finlayson et al. [17] explained the observation of glyoxal phosphorescence by postulating the decomposition of the dioxetane (II) by path h shown in Fig. 1. This path is not available to 3-methyl-1-butene unless methyl loss or migration occurs in the dioxetane (III), as the radical (IV) which would be formed following fragmentation of the dioxetane would not possess an O_2-abstractable hydrogen atom:

392
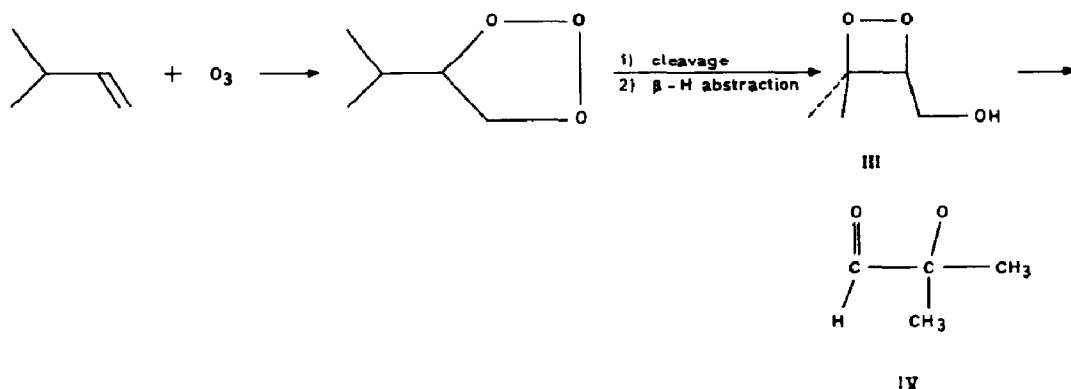
Therefore, no α-dicarbonyl phosphorescence would have been predicted for the reaction of O_3 with 3-methyl-1-butene on the basis of this postulate. Figure 10 clearly shows that α-dicarbonyl emission is present, with a maximum at 521 nm. Since identical results were obtained using 3-methyl-1-butene of either 99.0% or 99.9% purity, chemiluminescence due to the reaction of ozone with impurities is improbable. Furthermore, the observation of α-dicarbonyl emission in the absence of O_2, which has been confirmed recently by Schurath *et al.* [49] in the reaction of O_3 with isobutene [49], discounts the proposed necessary presence of O_2 for excited state α-dicarbonyl production. Clearly, some other mechanism is responsible for the production of the observed emission. As to the identity of the emitting species, the bandwidth (FWHM) is identical to that of glyoxal produced from the reaction of ozone with *trans*-2-butene, measured at the same spectral resolution. Since methylglyoxal emission (from the ozone–isobutene reaction, for example) exhibits a broader emission band, higher alkyl substituted α-dicarbonyls might also be expected to exhibit emission bands broader than that from glyoxal itself. It seems probable, therefore, that glyoxal is the emitting species.
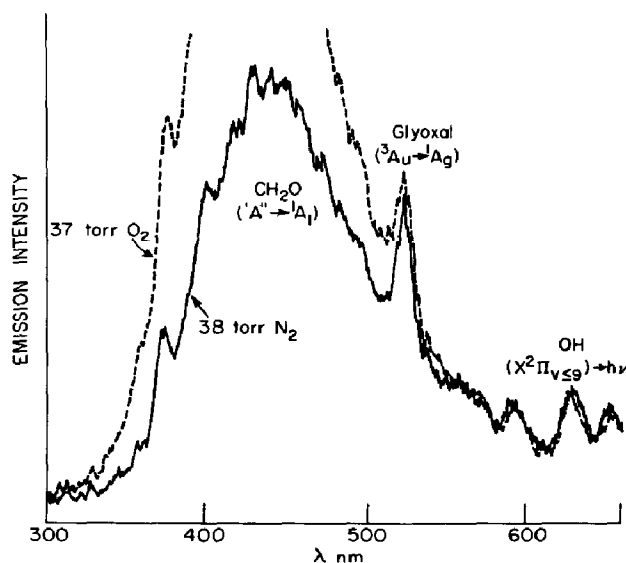
Fig. 10. Chemiluminescent spectra from the reaction of O_3 with 3-methyl-1-butene at total pressures of 38 Torr N_2 and 37 Torr O_2.

Of the currently proposed mechanisms for α-dicarbonyl formation none meets the necessary criteria of releasing sufficient exothermicity to yield excited state products and of operating in the presence of almost 40 Torr O_2.

The $H_2CO(^1A'')$ emission intensity of the reaction of ozone with 3-methyl-1-butene in O_2 is markedly enhanced over that in N_2 (Fig. 10). This effect can be rationalized if it is assumed that $HCHO(^1A'')$ is formed by the reaction of O_3 with the methyleneperoxy radical (3-methyl-1-butene being a terminal olefin). The effect of O_2 is possibly to "scavenge" radicals which

otherwise would react with, and remove, the methyleneperoxy radical. In addition, this explanation further assumes that the reaction of methyleneperoxy with O_2 is orders of magnitude slower than with O_3.

A similar oxygen-induced enhancement of formaldehyde emission intensity is observed in the reaction of O_3 with ethylene, propylene and 1,3-butadiene. It is difficult to reconcile this oxygen-induced enhancement of the formaldehyde emission with either the O'Neal and Blumstein [50] or the Finlayson et al. [17] mechanistic proposals.

(2) Since formaldehyde emission ($^1A''$ → $^1A_1$) is observed from the reaction of O_3 with ethylene, propylene, 1-butene, isobutene, cis- and trans-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene, at least two mechanisms for the formation of excited $HCHO(^1A'')$ must be operative. This follows from the fact that both terminal and internal olefins yield formaldehyde emission. Dioxetane decomposition [50] and α-carbonyl-hydroperoxide decomposition [53] can account for most of the observations related to formaldehyde emission from the above reactions. For propylene, these two mechanisms are as follows:
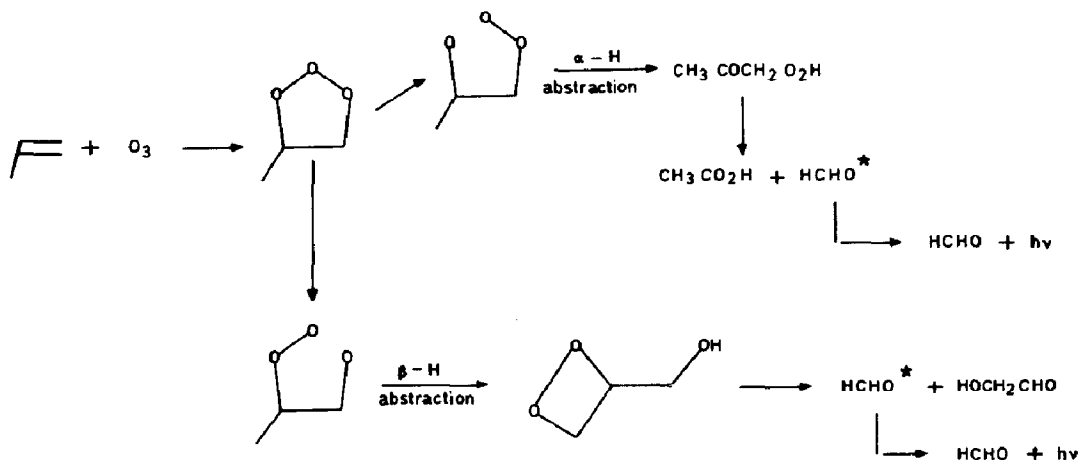
To test these proposed routes, formaldehyde emissions (A'' → $^1A_1$) were monitored from the reaction of ozone with the following olefins: 1,2-difluoroethylene, 3,3,3-trifluoropropylene, 1,1-dichloropropylene, acrolein, cyclopentene, 3-hexene and 4-octene.

The 3,3,3-trifluoropropylene and acrolein can only give excited formaldehyde by the α-hydrogen abstraction route, while 1,1-dichloropropylene can only give formaldehyde by the β-hydrogen abstraction route. Acrolein is potentially interesting because β-hydrogen abstraction might lead to the formation of excited CO_2, which might emit ($\lambda \approx 350$ nm) or decompose [63].

1,1- and 1,2-Difluoroethylenes

Previously unreported emissions were detected from these reactions, although Sheinson et al. [48] have recently observed emission from the reac-

tion of O_3 with C_2F_4, 1,1-$C_2H_2F_2$, and *cis*- and *trans*-1,2-$C_2F_2H_2$, with emission maxima occurring at 320 nm (C_2F_2) and 440 nm ($C_2H_2F_2$). These observations are in reasonable agreement with the present data on 1,1- and 1,2-$C_2H_2F_2$.

In O_2 (7.3 Torr and 38.5 Torr total pressures) and in N_2 (41 Torr total pressure) the reaction of ozone with 1,2-difluoroethylene gave a chemiluminescent spectrum characteristic of carbonyl $\pi^* \to n$ radiative transitions. However, the emission maximum at about 435 nm (Fig. 11) is red-shifted from that of formaldehyde (427 nm) or the formyl radical (362 nm). Of the plausible candidates for the species responsible for this emission carbonyl fluoride and formyl fluoride seem unlikely. The O—O band of formyl fluoride occurs at 266.8 nm [64], whereas the onset of emission in Fig. 11 occurs near 310 nm. Such a large gap between the onsets of absorption and emission would be unexpected owing to the similarity of the excited state geometry of HFCO to that of formaldehyde [64] which has overlapping emission and absorption. This same argument would apply even more strongly in the case of carbonyl fluoride whose onset of absorption occurs near 238 nm [65]. However, the geometry of the $A_2(A'')$ state of F_2CO is not known with certainty at the present time [65]. A third possible emitting species would be the FCO radical. The emission spectrum of this radical has not been reported previously, but good mirror symmetry with the absorption spectrum of matrix isolated FCO [66] is obtained when the unidentified emission spectrum is plotted on a wavenumber scale. The absorption spectrum has been confirmed in a flash photolysis study [67]. Formyl emission appears to be superimposed upon the suggested FCO continuum when the reaction is run at 7.7 Torr total pressure in N_2, as shown in Fig. 11. The absence of HCO emission in O_2 implies either that O_2 is an efficient quencher of HCO* or that O_2 removes the precursors to HCO* formation or both. Furthermore, the absence of HCO* emission in N_2 at 41 Torr total pressure, while the emission attributed to FCO remains essentially unaltered, suggests that HCO* is rapidly quenched by N_2 or that a chemically activated precursor is necessary for the production of HCO*.

A very weak, and as yet unidentified, chemiluminescence spectrum was obtained from the reaction of 1,1-difluoroethene with ozone at a total pressure of 6.9 Torr in O_2 (Fig. 11). In the absence of O_2 this reaction also produces the emission we have tentatively ascribed to FCO at a somewhat lower intensity than from the reaction of O_3 with 1,2-difluoroethylene. This spectrum is shown in Fig. 11 so that a comparison with the chemiluminescent spectrum from the O_3 + HFC=CHF reaction may be made. The reason that O_2 completely quenches FCO emission from the reaction of O_3 with H_2C=CF_2 but does not have such a pronounced effect upon the O_3 + HFC=CHF reaction is unclear at present.

Electronically excited $OH(A^2\Sigma^+)$ and vibrationally excited $OH(X^2\Pi)_{v \leqslant 9}$ are also produced in the reactions of ozone with the difluoroethylenes, as with hydrocarbon olefins, and the resulting emission spectra can readily be identified in Fig. 11.
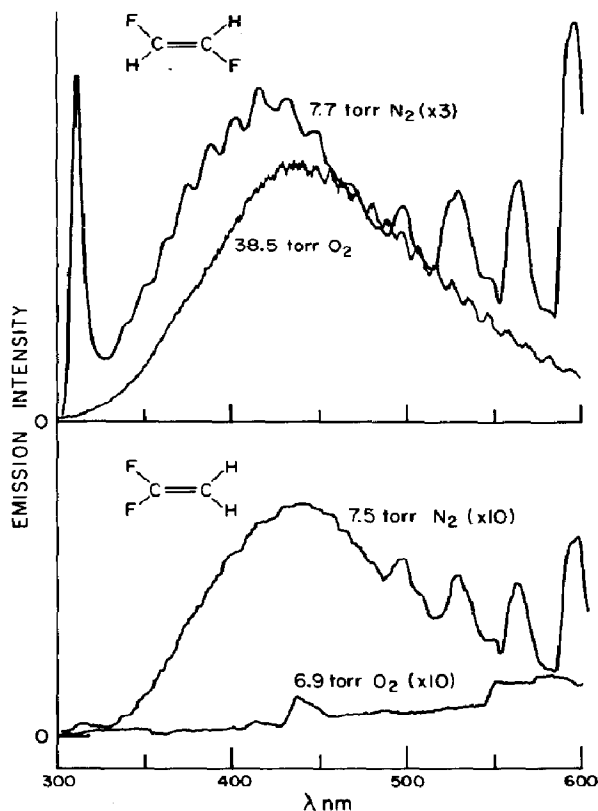
Fig. 11. Chemiluminescent spectra from the reactions of O_3 with 1,2- and 1,1-difluoro-ethylene.

3,3,3-Trifluoropropene

A third fluorinated olefin, 3,3,3-trifluoropropylene, was reacted with ozone at varying pressures of N_2 or O_2. No emission was detectable when the reaction was carried out in O_2. At 14.4 Torr total pressure in N_2 only very weak $OH(A^2\Sigma^+)$ and $OH(X^2\Pi)_{v < 9}$ emission was seen. The observed behavior probably results from a very slow rate constant for the initial attack of O_3 upon the olefin because of its electron-deficient double bond. However, since excited OH was formed, albeit in relatively small quantities, but $CH_2O(^1A'')$ was not formed in detectable quantities, this may be a result of the lack of an abstractable hydrogen at the 3-position. Such an abstractable hydrogen is required for production of an intermediate dioxetane, the decomposition of which yields electronically excited CH_2O in the O'Neal–Blumstein gas phase ozonolysis mechanism. The fact that OH emission was observed shows that the presence of vinyl hydrogens is sufficient for H atom production.

1,1-Dichloropropylene

The final halosubstituted olefin studied was 1,1-dichloropropylene. As with 3,3,3-trifluoropropene no emission was detectable from the ozonolysis of this compound in O_2. In N_2, however, at a total pressure of 6.4 Torr, strong

chemiluminescence was observed. The spectrum of this emission is shown in Fig. 12. All the emitting species that result from the reaction of O_3 with propylene are present, although the α-dicarbonyl (probably glyoxal) emission at 523 nm is barely identifiable because of the strong Meinel band at 527 nm. This demonstrates that terminal vinyl hydrogen atoms are not necessary for production of any of the observed excited species. What is remarkable about this spectrum is that the lack of definition of the formaldehyde bands normally observed from ozone–olefin reactions run at less than 10 Torr is not apparent here. The relatively well-resolved CH_2O bands show the emitting state to be rotationally cold. Further study on this system would be necessary in order to clarify the factors which govern the production of rotationally cold $HCHO(^1A'')$.
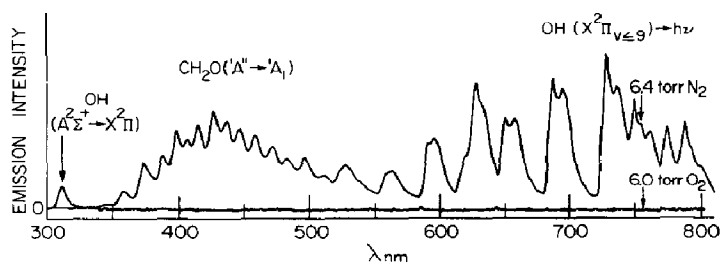
Fig. 12. Chemiluminescent spectra from the reaction of O_3 with 1,2-dichloropropylene at total pressures of 6.4 Torr N_2 and 6.0 Torr O_2.

Cyclopentene

Production of $OH(A^2\Sigma^+)$ and $(X^2\Pi)_{v \leqslant 9}$ from the ozone–cyclopentene reaction is very efficient relative to other ozone–olefin reactions. Identification of glyoxal as the α-dicarbonyl emitter is confirmed by the presence of the 555 and 575 nm bands which are clearly evident in the spectrum obtained from the reaction run in O_2 (Fig. 13).
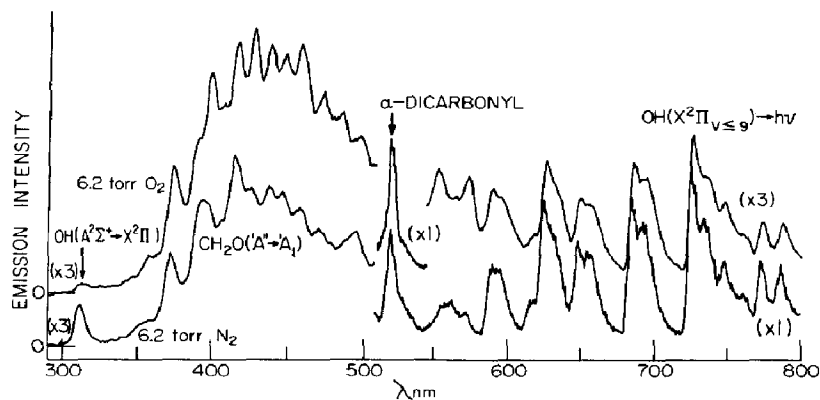

Fig. 13. Chemiluminescent spectra from the reaction of O_3 with cyclopentene at total pressures of 6.2 Torr O_2 and 6.2 Torr N_2.

Some of the emission bands in the 350 - 500 nm region are assignable to $H_2CO(^1A'')$, yet no mechanism discussed in connection with previous ozone–olefin reactions can account for its production. That is, β-H abstraction, if feasible within the constraints imposed by the cyclopentane ring of the biradical intermediate, would ultimately lead to the formation of

$$
\underset{\text{HCCH}_2\text{CH}_2\text{CHCH}}{\overset{\text{O}\quad\ \ \text{OH}\quad\ \text{O}}{\overset{\|\qquad\ \backslash\qquad\|}{}}}
$$
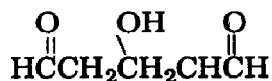
None of the reaction pathways considered for terminal olefins would apply because cyclopentene possesses an internal double bond. The apparent enhancement of the formaldehyde emission in O_2 relative to the emission in N_2 seems to rule out radical–radical processes if it is assumed that O_2 would scavenge possible radical precursors. This observation of formaldehyde emission from a chemical system in which the emission is not accounted for by any of the presently proposed mechanisms is intriguing and suggests that great care must be taken in drawing mechanistic conclusions based on prior proposals.

An additional unique feature of the chemiluminescence compared with that produced from the reaction of ozone with aliphatic olefins is the appearance of emission bands in the same spectral region as, but not assignable to, formaldehyde. These bands are particularly noticeable in the spectrum obtained from the reaction run in N_2 and occur near 394 and 416 nm. Their effect is also seen in the spectrum obtained from the reaction run in O_2 in that their presence caused the intensity distribution of the formaldehyde bands to be unlike that observed from reactions such as ozone–ethylene or ozone–1,3-butadiene which produce only formaldehyde emission in this spectral region. These same bands appear to be present in the chemiluminescence spectrum of the reaction of ozone with crotonaldehyde and acrolein (see later).

Acrolein

The chemiluminescent spectrum of the reaction of O_3 with acrolein run in N_2 at 7.9 Torr was very similar to that of the ozone–crotonaldehyde reaction and showed emission from $OH(X^2\Pi)_{v<9}$, $OH(A^2\Sigma^+)$, glyoxal (^3A_u) and $CH_2O(^1A'')$ (Fig. 14). The reaction run in O_2 (8.7 Torr) quenched all emissions. However, when only 16% O_2 in N_2 was used, although formaldehyde emission essentially disappeared, a residual emission remained (Fig. 14) having band maxima at 394 and 416 nm. In N_2 the effect of the underlying bands was to distort the shape and position of the formaldehyde bands. These same band maxima were observed from the ozone–cyclopentene and ozone–crotonaldehyde reactions as mentioned above, and the particular wavelengths of these maxima suggest that the emission may be due to $CO_2(^1B_2)$.

The remarkably efficient quenching effect of O_2 upon all emissions is analogous to the behavior noted for the ozone–3,3,3-trifluoropropylene and ozone–1,1-dichloropropylene reactions.
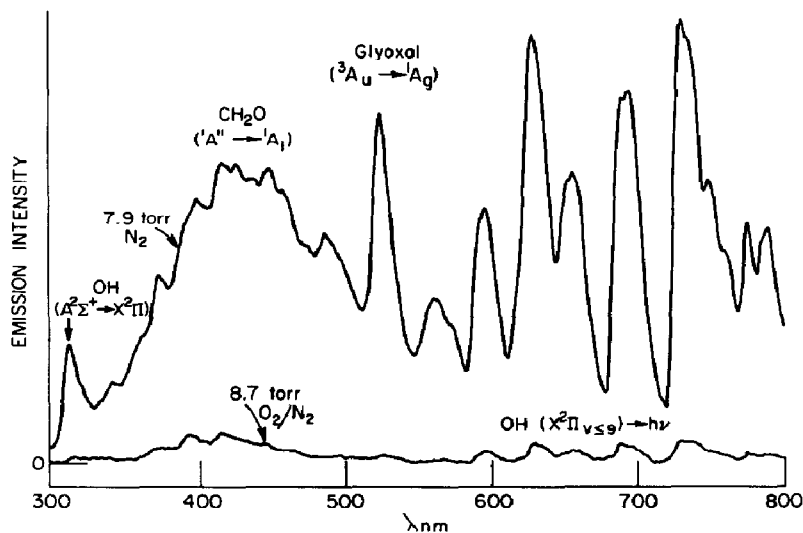
Fig. 14. Chemiluminescent spectra from the reaction of O_3 with acrolein at total pressures of 7.9 Torr N_2 and 8.7 Torr O_2/N_2 ($O_2:N_2 = 1:5.3$).

trans-3-*Hexene and* trans-4-*octene*

The effect of increasing chain length in linear symmetric olefins upon the ozonolysis chemiluminescence was studied using trans-3-hexene and trans-4-octene as model compounds. The spectrum obtained from a run using a 4:1 ratio of trans-3-hexene to ozone in N_2 at 6.7 Torr is shown in Fig. 15. Identifiable emissions are those from $H_2CO(^1A'')$ at 340 - 500 nm, an unspecified α-dicarbonyl compound at 522 nm and $OH(X^2\Pi_i)_{v < 9}$ at 550 - 800 nm. The spectra were also obtained from reactions run with a 2:1 excess of O_3 to trans-3-hexene in 6 Torr N_2 and O_2. An $OH(A^2\Sigma^+)$ emission was observed from the reaction run in N_2 but not in O_2. Formaldehyde emission intensity was identical in both cases, but reduced relative to the run using excess olefin. An α-dicarbonyl emission was detectable from the O_2 run and similarly reduced relative to the excess olefin run. Intense Meinel band emission was observed from the reaction run in N_2 such that α-dicarbonyl emission, if present, was obscured. When run in O_2, the Meinel band emission intensity was reduced by a factor of 8.
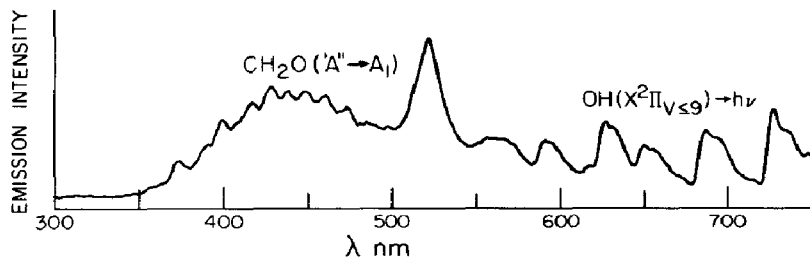

Fig. 15. Chemiluminescent spectra from the reaction of O_3 with trans-3-hexene at a total pressure of 6.7 Torr N_2.

Chemiluminescence spectra were obtained from the reactions of ozone with *trans*-4-octene under conditions similar to the latter two *trans*-3-hexene runs. In N_2 the $OH(A^2\Sigma^+)$ emission intensity was essentially the same as that from the ozone–hexene reaction but was not detectable in O_2. In N_2 the $CH_2O(^1A'')$ emission intensity was only 60% of that from the ozone–hexene reaction and was reduced by another factor of 2 in O_2. An α-dicarbonyl emission was observed from the reaction run in O_2 and was about half as intense as that from the ozone–hexene reaction. Meinel band emission intensity was equal to that measured from the latter reaction when run in N_2. The use of O_2 reduced this intensity by a factor of 20.

(3) Because the production of H atoms during ozone–olefin reactions appears to be complex [17], the OH Meinel band emission from various deuterated propylenes was monitored to see whether additional mechanistic information could be deduced. The compounds used were $CH_2=CHCD_3$, $CH_2=CDCH_3$, $CD_2=CHCH_3$ and $CD_2=CDCH_3$. The OD emission analogous to the OH Meinel band emission has not been detected but is expected to occur at $\lambda > 850$ nm [17].

In addition, a series of deuterated propylenes were reacted with O_3 at a total pressure of 19.5 Torr in O_2 to examine the effect of the position of deuteration on the emission intensity from other excited species. The compounds studied were 2-propylene-d_1, 1,1-propylene-d_2, 1,1,2-propylene-d_3, 3,3,3-propylene-d_3 and propylene-d_6. In all cases spectra were obtained under identical conditions with propene-h_6 used for comparison purposes either immediately before or after the deuterium substituted propylene runs.

The intensities of the specific emissions were normalized to those observed from the ozone–propylene-h_6 reaction and are listed in Table 1.

TABLE 1

Relative intensities of the observed emission resulting from the reaction of ozone with deuteropropylene isomers

Olefin	CH_2O CD_2O $DCHO$	$(HCO)_2$ $HCOCOD$ $(DCO)_2$	$OH(X^2\Pi_i)_{v<9}$
$CH_2=CDCH_3$	0.9	1.2	0.8
$CD_2=CHCH_3$	1.7	0.9	0.75
$CD_2=CDCH_3$	1.4	1.2	0.50
$CH_2=CHCD_3$	2.0	$< 0.45^a$	0.9
$CD_2=CDCD_3$	2.0	0.45	0.0
$CH_2=CHCH_3$	1.0	1.0	1.0

[a] Since the mass flow of 3,3,3-propene-d_3 was greater than that of propene at the time the glyoxal spectral region was scanned in each case and α-dicarbonyl emission intensity is roughly proportional to propene concentrations, only an upper limit may be set.

Where necessary and determinable, the intensities were corrected for differing mass flow of olefin over the appropriate spectral ranges before normalization.
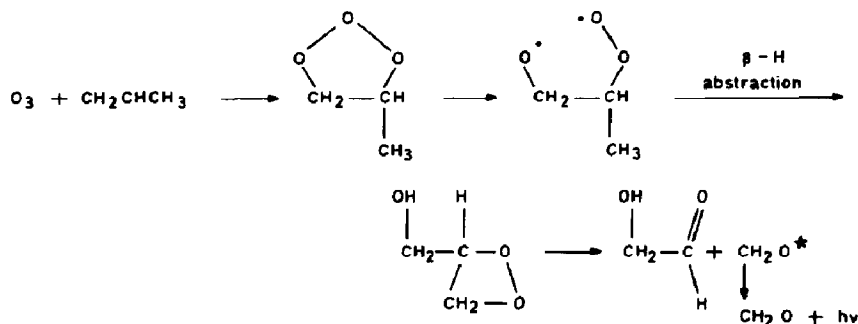
OH, OD($A^2\Sigma^+$)

The observed emission intensities of the electronically excited OH and OD radicals were barely above the level of detectability at the pressure used, and hence no conclusions about the effect of deuteration on emission intensities can be drawn.

H_2CO, HDCO, D_2CO($^1A''$)

The only isotopically substituted formaldehyde possible from the reaction of O_3 with propylene-d_6 is D_2CO, and its chemiluminescence spectrum is presented in Fig. 16 along with that for the reaction of O_3 with propylene-h_6. The intensity is double that of H_2CO from the reaction of O_3 with propylene (Table 1), and the rotational temperature of the emitting D_2CO is less than that of the H_2CO such that the vibrational progressions are more clearly defined. The fluorescence quantum yield of D_2CO($^1A''$) must be at least twice that of H_2CO($^1A''$) since any intramolecular D-abstraction leading to D_2CO would reduce the rate of production relative to that of H_2CO. No emission from D_2CO($^3A''$) was detected.

If the reaction pathway proposed by O'Neal and Blumstein [50] for production of electronically excited formaldehyde,

$$O_3 + CH_2CHCH_3 \longrightarrow \underset{\substack{| \\ CH_3}}{CH_2 - CH} \overset{\displaystyle O}{\underset{\displaystyle O}{\diagdown\diagup}} \longrightarrow \underset{\substack{| \\ CH_3}}{CH_2 - CH} \overset{\displaystyle \cdot O}{\underset{\displaystyle O}{\diagdown\diagup}} \xrightarrow{\substack{\beta - H \\ \text{abstraction}}}$$

$$\underset{\substack{\diagup \quad \diagdown \\ CH_2 - O}}{\overset{\substack{OH \quad H \\ | \quad |}}{CH_2 - C - O}} \longrightarrow \underset{\substack{\diagdown \\ H}}{\overset{\substack{OH \quad O \\ | \quad \diagup\!\diagup}}{CH_2 - C}} + CH_2O^* \quad\downarrow\quad CH_2O + h\nu$$

represents the actual mechanism, then the reaction of ozone with 3,3,3-propene-d_3 should produce exclusively D_2CO($^1A''$). The chemiluminescent spectrum from this reaction showed that this was the case, although minor CH_2O may not be excluded.

The enhancement of the formaldehyde emission from the O_3 + CD_2CHCH_3 and CD_2CDCH_3 reactions (intermediate between the O_3 + CH_2CHCH_3 and CD_2CDCD_3 reactions) may reflect the contribution of deuteromethylene groups to the total formaldehyde emission intensity. Although incorporation of the deuteromethylene groups in the product formaldehyde may be a minor process, the at least double fluorescence quantum yield of D_2CO relative to H_2CO would result in a generally enhanced emission intensity. This hypothesis is supported by the fact that the spectra of $CD_2 = CD - CH_3$ and $CD_2 = CH - CH_3$ showed apparent superposition of the D_2CO and H_2CO fluorescence spectra.
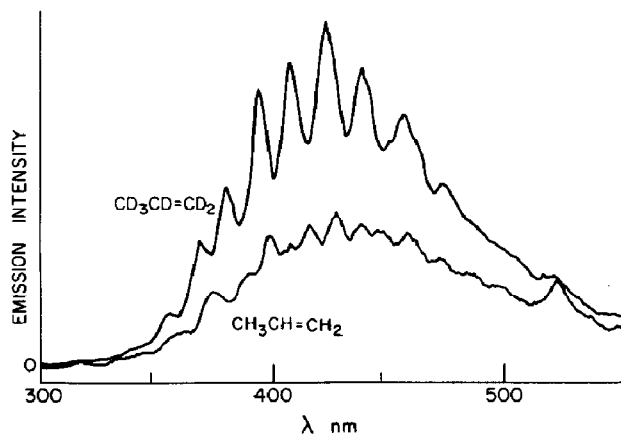
Fig. 16. Chemiluminescent spectra ($300 < \lambda < 500$ nm) from the reactions of O_3 with propylene-h_6 and propylene-d_6 at a total pressure of 19.5 Torr O_2.

The reaction of ozone with 2-propene-d_1 almost certainly leads to the production of $H_2CO(^1A'')$ and possibly $HDCO(^1A'')$. The lack of well defined vibrational structure in the chemiluminescence spectrum means that there is little information concerning the identity of the emitting formaldehyde isomer. Since the emission intensity is not significantly different than that from the ozone–propene reaction, it is reasonable to conclude that $H_2CO(^1A'')$ production predominates.

(HCO)$_2$, HCOCOD, (DCO)$_2$(^{3}A$_u$)

The spectral resolution (5 - 8 nm) used in this study was chosen as a compromise between obtaining adequate signal strength to complete the spectral scans before the liter quantities of olefins were consumed and obtaining sufficient resolution to distinguish between the isotopically substituted emitting species. Unfortunately, in the case of the glyoxal emission the spectral resolution used did not allow distinction between the glyoxal isomers to be made. Hence no conclusions can be drawn as to whether the variations in glyoxal emission intensities given in Table 1 are due to a kinetic isotope effect or to differing phosphorescence quantum yields for the emitting species.

OH($X^2\Pi_i$)$_{v < 9}$
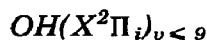
The OH Meinel band emission from ozone–olefin reactions has been shown [17] to result from the reaction of H atoms with ozone:

$$H + O_3 \rightarrow O_2 + OH(X^2\Pi_i)_{v < 9}$$
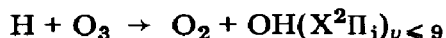
In the spectral region examined here $OD(X^2\Pi_i)$ does not emit. The mechanism for production of H atoms from ozone–olefin reactions is uncertain although several possibilities have been proposed [17, 50, 52, 53].

The data presented in Table 1 show that vinyl deuterium substitution reduces H atom production to a greater extent than does 3,3,3-trideutero-substitution. That half the OH Meinel band intensity remains upon deuteration

of all three vinyl positions (1,1,2-propene-d_3) demonstrates that H atoms may be produced from either terminus, and perhaps the 2-position (since ozone–1,1,3,3,3-propene-d_5 was not studied). The inescapable conclusion is that H atoms are produced via more than one reaction pathway. Thus, because of the many possible mechanisms available for H atom production from ozone–olefin reactions, no specific reaction pathways may be favored on the basis of chemiluminescence.

Conclusions

From the above results it can be seen that the present theories of ozone–olefin reactions do not entirely predict the chemiluminescing species observed. In some respects this is not entirely surprising, as in most cases (except for OH Meinel band emission) the emission processes are only a very small fraction of the total reaction pathways [17]. Thus at this time a more vigorous test of the proposed mechanisms via a stable product analysis study under a variety of conditions is required. Such studies are being carried out in this laboratory and by Niki and coworkers [22].

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