

volume necessary at the cost of the interaction energy for the second rotamer. For a normal hydrocarbon a gauche rotamer is about $0.5 \text{ kcal mol}^{-1}$ above that for a trans rotamer.²² The value we observe could indicate an increased rigidity of a hydrocarbon chain when it is packed in a liquid crystal. Results somewhat similar to these have been obtained in a more indirect manner from spin label work, particularly that of Seelig and his coworkers.^{23,24}

Conclusion

In this study we have examined some of the properties of the model membrane system based on decylammonium chloride. Proton nuclear magnetic resonance in conjunction with the anisotropic properties of the middle soap region of this cationic surfactant has enabled us to determine the carbon and hydrogen positions in the acetate ion. These structural data in conjunction with the deuterium nmr spectrum from the

(22) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

(23) J. Seelig, H. Limacher, and P. Bader, *J. Amer. Chem. Soc.*, **94**, 6364 (1972).

(24) H. Limacher and J. Seelig, *Angew. Chem., Int. Ed. Engl.*, **11**, 920 (1972).

fully deuterated ion were then used to determine the quadrupole coupling constant for the deuteriums of the perdeuteriomethyl group of the ion.

Deuterium magnetic resonance studies of the specifically deuterated 1,1,1,2,2-pentadeuteriodecylammonium ion were able to describe the microdegrees of order of the headgroups in the electrical double layer. The motions of the headgroups are considerably restricted and can be accounted for in terms of oscillations of the segment axis of the $-\text{CD}_2\text{ND}_3^+$ group, rotation of the $-\text{ND}_3^+$ group, and finally rotations about the C-N bond which probably involve gauche conformers in the hydrocarbon chain.

Assuming the superstructure of the phase to be of the cylindrical type, the lateral diffusion of the detergent ions or rotation of the cylinders themselves can be accounted for in the experimental degrees of orientation. The methodology developed for treating this system can be generalized to other systems and has the advantage that unlike results obtained from spin labels there is unlikely to be any perturbation of the system under study. Application of this technique to other model membrane systems whether of lamellar or cylindrical type can therefore be expected to be particularly rewarding.

Low-Pressure Gas-Phase Ozone-Olefin Reactions. Chemiluminescence, Kinetics, and Mechanisms

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Abstract: Chemiluminescence from $\text{HCHO}(^1\text{A}'' \rightarrow ^1\text{A}_1)$, $\text{OH}(X^2\pi_i)_{v' \leq 9}$, and $\text{OH}(A^2\Sigma^+)$ has been observed in the gas-phase reactions of 2% O_3 in O_2 , N_2 , or He with a series of simple olefins in a flow system at room temperature and at total pressures of 2–10 Torr. The vibration-rotation emission from $\text{OH}(X^2\pi_i)_{v' \leq 9}$ was virtually identical with OH Meinel band emission from reaction 2, $\text{H} + \text{O}_3 \rightarrow \text{OH}(^2\pi_i)_{v' \leq 9} + \text{O}_2$, confirming that H atoms are formed in O_3 -olefin reactions under these experimental conditions. In the presence of O_2 , glyoxal phosphorescence was identified in the 2-butene (cis or trans) reaction and methylglyoxal phosphorescence was tentatively identified from the reactions of isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene with ozone. 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 to be 10^{-7} for $\text{HCHO}(^1\text{A}'' \rightarrow ^1\text{A}_1)$ and 10^{-5} quanta for $(\text{CHO})_2(^3\text{A}_u \rightarrow ^1\text{A}_g)$ 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 consumed, indicating that the formation of vibrationally excited OH is a surprisingly efficient process under these conditions. In the ethylene, cis-2-butene, and isobutene reactions, the time decay of light emission from each excited species was exponential in O_2 but nonexponential in N_2 or He, with increased emission intensities occurring at reaction times $\lesssim 0.1$ sec in the latter case. Rate constants, determined from the loss of O_3 in both O_2 and N_2 as diluents, assuming 1:1 stoichiometry, were a factor of 2–5 times greater in N_2 . In 10 Torr of O_2 , the measured rate constants for the ethylene, cis-2-butene, and isobutene reactions respectively were $1 \pm 1 \times 10^3$, $6.3 \pm 1.9 \times 10^4$, and $5.4 \pm 2.3 \times 10^3 \text{ l. mol}^{-1} \text{ sec}^{-1}$. Major products of the reaction of cis-2-butene with ozone in either O_2 or N_2 as the carrier gas were, in addition to acetaldehyde, 2-butanone, possibly from the OH-cis-2-butene reaction, and methyl vinyl ketone which was observed only in oxygen. The results are discussed in terms of the O'Neal-Blumstein theory of gas phase ozone-olefin reactions and the possible role of these reactions in photochemical smog formation is considered.

Extensive mechanistic investigations of the liquid-phase reactions of ozone with olefins have identified many of the reaction intermediates and have established the Criegee zwitterion mechanism as a major reaction pathway.¹⁻⁴ Until recently, the Criegee mech-

anism has also been widely assumed to apply to the initial steps of the gas-phase reaction. However, in the gas phase at room temperature, unimolecular decom-

(1) L. Long, *Chem. Rev.*, **27**, 437 (1943).

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(4) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968), and references therein.

position or rearrangement of the "zwitterion" (more likely a biradical in the gas phase) is expected to predominate over recombination with the carbonyl fragment.^{5,6} Although several reports⁵⁻¹⁰ of gas-phase products, including secondary ozonides,^{6,9} are consistent with this mechanism, it fails to explain the formation of free radical intermediates^{11,12} in low-pressure (~ 2 Torr) ozone-olefin reactions and of "unusual" ozonolysis products, both at low¹² and high total pressures.^{7,8,13,14}

Recently, evidence on the nature of certain excited intermediates in gas-phase ozone-olefin reactions has appeared. Thus, chemiluminescence from the room-temperature gas-phase ozone-ethylene reaction at atmospheric pressure was first observed by Nederbragt, *et al.*,¹⁵ and further investigated by Warren and Babcock¹⁶ and Hodgeson and coworkers.¹⁷⁻¹⁹ Subsequently, studies^{11,20-22} in our laboratories showed that at low pressures (~ 1 Torr) all simple olefins chemiluminesce on reaction with 2% O_3/O_2 . Meinel band emission from vibrationally excited OH radicals was observed for the first time in these oxidations, and formaldehyde fluorescence was tentatively identified¹¹ in the reactions of ethylene, propylene, and 1-butene.

Concurrently, on the basis of thermochemical-kinetic calculations, O'Neal and Blumstein²³ proposed alternatives to the gas-phase Criegee mechanism. These involve internal hydrogen abstractions of the initial molozonide in addition to its decomposition to the Criegee fragments. Their mechanism rationalizes most of the "unusual" products observed in previous studies, as well as the production of chemiluminescence.

Reported here are the results of further detailed studies of low-pressure ozone-olefin reactions, using more sensitive and more quantitative spectroscopic techniques to provide the requisite resolution for conclusive identification of the light-emitting species and to

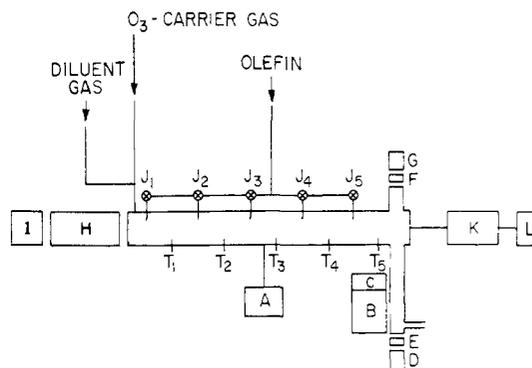


Figure 1. Schematic of apparatus used in chemiluminescence and kinetic studies; A, pressure transducer; B, EMI 9558A photomultiplier; C, optical filters; D, pen-ray mercury lamp; E, Corning 7-54 filter; F, 254 ± 26 nm filter; G, RCA IP28A photomultiplier; H, 0.3-m McPherson scanning monochromator; I, photomultiplier; K, Carle gas sampling valve; L, gas chromatograph; J_1 - J_5 , inlet jets; T_1 - T_5 , thermistors.

permit estimates to be made of their absolute rates of light emission. Additionally, the kinetics of the light intensities and of ozone decay, measurement of the self-heating of the gas mixture in these exothermic reactions, analysis of the major stable products, and the effects on these parameters of replacing the oxygen carrier gas by nitrogen are presented. This evidence, along with our recent results on intermediate species obtained using a photoionization mass spectrometer¹² (hereafter referred to as PMS), is discussed in terms of the O'Neal-Blumstein mechanism.

Experimental Section

Apparatus. The flow system used in these studies is shown schematically in Figure 1. Along the length of the Pyrex flow tube (5-cm i.d., 1-m length) were five substrate inlet jets (J_1 - J_5) and five Pyrex bead-type thermistors (T_1 - T_5) (Fenwal Electronics Inc.) which had been calibrated against a quartz thermometer. Pyrex or quartz windows were attached to the ends of the flow tube using Teflon-lined end couplings. Flow tube pressure was measured with a Statham 0-5 psia transducer (A) calibrated against an MKS Baratron gauge. Flow tube pressures were not corrected for pressure drop along the flow tube, as the Poiseuille equation predicts a pressure drop of $\sim 1 \mu$, $\leq 0.1\%$ of the total pressure. The flow tube was connected to a conventional high-vacuum line via Teflon stopcocks and Teflon-lined ball and socket joints. Where appropriate, a fluorinated grease (Krytox 240AC) was used to minimize O_3 decomposition. The flow tube was periodically cleaned by baking overnight at 565° .

For studying the kinetics of the chemiluminescent emission of individual excited species, appropriate optical filters (C) were used to isolate the emission which was detected by a cooled EMI 9558A photomultiplier (B). The following optical filters were used: (1) for $HCHO(^1A'' \rightarrow ^1A_1)$, cutoff filters isolating the $373 < \lambda < 473$ nm region; (2) for $OH(X^2\pi_i)_{v' \leq 9}$ Meinel band emission, a cutoff filter transmitting $\lambda > 555$ nm; (3) for $OH(A^2\Sigma^+ \rightarrow X^2\pi_i)$, a 317 ± 6 nm interference filter; and (4) for the emissions at 517-520 nm, cutoff filters isolating the $510 < \lambda < 555$ nm region.

The kinetics of O_3 consumption were followed by monitoring the 253.7-nm absorption of O_3 using a pen-ray lamp (D) and RCA 1P28A photomultiplier (G). The filter combination (E,F) isolated the 253.7-nm line and reduced scattered light at other wavelengths.

Chemiluminescent emission spectra were scanned using a McPherson 0.3-m scanning monochromator (H) and a cooled photomultiplier (I) (EMI 9684B, 9558A or 9659QB) whose output was amplified by a lock-in amplifier (PAR Model 120, operated at 360 Hz) or a photon counter (SSR Instruments Model 1120 amplifier discriminator, and Model 1105 data converter console) and displayed on a potentiometric recorder. To enhance the observed emission intensities, a plane mirror was placed opposite the monochromator at the downstream end of the flow tube.

Gas chromatographic analysis of the *cis*-2-butene-ozone reac-

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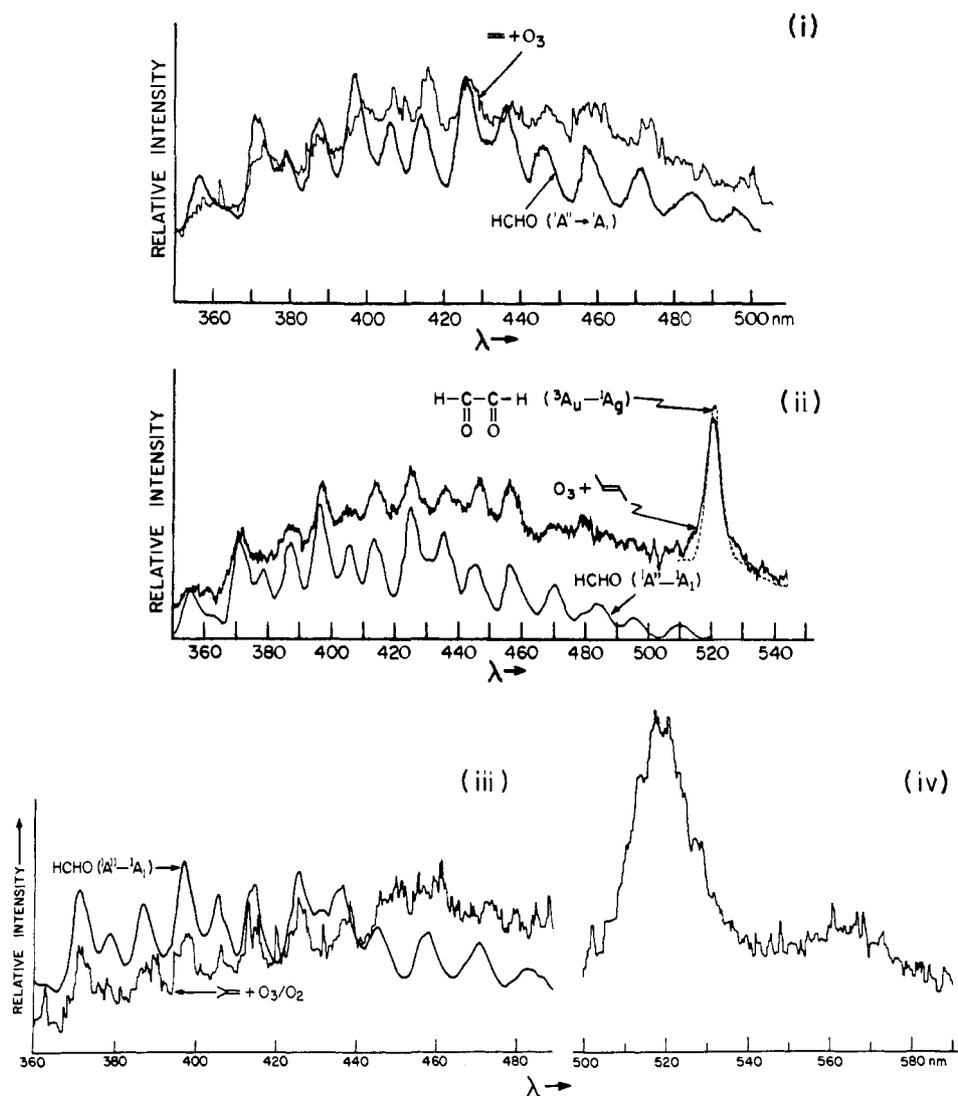


Figure 2. Chemiluminescent emission spectra in the visible region from the reaction of 2% O_3/O_2 with: (i) ethylene, total pressure 4.5 Torr, spectral slit width 3.2 nm; (ii) *trans*-2-butene, total pressure 3.5 Torr, spectral slit width 2.5 nm; (iii) isobutene, total pressure 4.4 Torr, spectral slit width 3.2 nm; (iv) isobutene, total pressure 4.4 Torr, spectral slit width 1.9 nm; (i-iii) $HCHO(^1A'' \rightarrow ^1A_1)$, total pressure 4.9 Torr, spectral slit width 2.5 nm; (ii) $(CHO)_2(^3A_u \rightarrow ^1A_g)$, total pressure 1.33 Torr, spectral slit width 0.45 nm.

tion was carried out using a Carle gas sampling valve (K) with 5 cm^3 sample loops attached to a Varian Aerograph Model 1200 gas chromatograph (L) with a flame ionization detector. The columns used were a 10 ft by $1/8$ in. 20% SE-30 column on 6/8 firebrick, operated at room temperature, and a 10 ft by $1/8$ in. 10% β,β -oxydi-propionitrile column, on 80/100 HMDS Chromosorb P, operated at 90°. Products were identified by comparison of their retention times to those of authentic compounds introduced into the Carle valve as a mixture with air.

O_3 /diluent and substrate flow rates were measured using calibrated flowmeters. Flow rates were typically 20–30 $\mu mol\ sec^{-1}$ of olefin and $\sim 130\ \mu mol\ sec^{-1}$ of the O_3 /diluent gas mixture at total flow tube pressures of 2–10 Torr. Linear flow velocities were $\sim 80\ cm\ sec^{-1}$ corresponding to a mean flow tube residence time of $\sim 1.3\ sec$.

The absolute rate of light emission from individual emitting species was determined by comparison²⁴ of the light intensity in the appropriate wavelength region from the $O-NO$ reaction, I_{O-NO} , to that from the ozone-olefin reaction, I_{O_3-OL} , where

$$I_{O-NO} = k_s[O][NO] \quad (I)$$

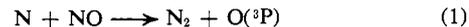
and

$$I_{O_3-OL} = k_x[O_3][olefin] \quad (II)$$

(24) A. Fontijn, C. B. Meyer, and H. I. Schiff, *J. Chem. Phys.*, **40**, 64 (1964).

k_s and k_x are the respective absolute rates of light emission in that wavelength region.

$O(^3P)$ atoms were generated by the microwave discharge of N_2 and subsequent titration of the N atoms by nitric oxide²⁵



with the $O(^3P)$ atom concentration being obtained from the end point of the titration. The 10.3% NO/N_2 was passed through a trap at Dry Ice temperature containing Linde Molecular Sieve 13X to remove any NO_2 and H_2O present.

The concentrations of O_3 and olefin were calculated, assuming 1:1 stoichiometry, from their initial concentrations using the measured rate constant for O_3 decay under these experimental conditions and the reaction time to the observation port.

Then, using the experimentally determined values of I_{O-NO} and I_{O_3-OL} and the known value of k_s ,²⁴ k_x was calculated. The total rate of light emission from that emitting species was then determined from the fraction of the total light emission from that excited species transmitted by the filter. For $HCHO(^1A'' \rightarrow ^1A_1)$ this fraction, isolated using a $430 \pm 11\ nm$ interference filter, was measured from its photoexcitation emission spectrum by planimetry. Similarly, in the *cis*-2-butene reaction, the rate of light emission from glyoxal from 510 to 555 nm, isolated using cutoff filters, was measured and the fraction this comprised of the total emission was

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calculated from the photoexcitation emission spectrum. It was assumed that at these total pressure no glyoxal fluorescence would occur due to rapid intersystem crossing from the singlet to the triplet state.²⁶⁻²⁸

The total OH Meinel band emission which extends to 4.5 μ^29 could not be recorded in this study due to instrumental limitations. Therefore, the intensity of a fraction of the (9,3) band was measured, and the total rate of light emission in the (9,3) band was calculated from the known transmission characteristics of the filter.

Chemicals. Ethylene, *cis*-2-butene, and isobutene (Matheson Research Grade $\geq 99.8\%$) were used without further purification. Gas chromatographic analysis of these olefins showed no detectable impurities. 2-Butene-*d*₆ (mixture of *cis* and *trans*) and isobutene-*d*₆ (Merck Sharp and Dohme, with stated D atom purities of $\geq 98\%$ and $\geq 99\%$, respectively) were used as received.

Ozone ($\sim 2\%$ in O₂) was prepared from O₂ (Matheson ultra-high purity) using a Welsbach ozonator Model T-408. O₃/N₂ or O₃/He (both containing $\leq 0.2\%$ O₂) were prepared by selective absorption of O₃ on silica gel^{30, 31} at -78° followed by elution with the diluent gas (N₂ or He).

H₂ ($\geq 99.999\%$), He ($\geq 99.95\%$), and N₂ ($\geq 99.95\%$) were used as received. H atoms were generated by methods described previously.¹¹

Formaldehyde was prepared from paraformaldehyde (Matheson Coleman and Bell) by the method of Spence and Wild.³² Acetaldehyde (Matheson Coleman and Bell), acetone (Mallinckrodt Spectra Grade), and biacetyl (Matheson Coleman and Bell) were thoroughly degassed at liquid nitrogen temperature and used without further purification. Glyoxal was prepared from glyoxal trimer (Matheson Coleman and Bell) by heating a mixture of trimer and P₂O₅ and collecting the glyoxal distillate in a liquid nitrogen trap. Volatile impurities in the glyoxal were removed by degassing at Dry Ice temperature.

Results

Identification of Chemiluminescing Species. Electronically excited formaldehyde, HCHO(¹A'), has now been confirmed as a chemiluminescing species common to all the ozone-olefin reactions that were studied at sufficient resolution to resolve the vibrational structure. Typical chemiluminescent emission spectra ($350 < \lambda < 600$ nm) are shown in Figure 2; also shown for comparison is the formaldehyde fluorescence excited by tesla coil discharge³³ and recorded with the same detection system.

The reactions of *cis*- and *trans*-2-butene with ozone have identical chemiluminescent emission spectra, an example of the latter being shown in Figure 2ii. The 520-nm peak from these reactions is assigned to glyoxal phosphorescence (³A_u \rightarrow ¹A_g) by comparison with the (0,0) band obtained by photoexcitation of glyoxal vapor at 430 ± 11 nm. The remaining vibrational bands of the triplet system^{34, 35} are obscured at these pressures by the much stronger Meinel band emission of the OH-(X² π_i)_{v' \leq 9} radical¹¹ (referred to hereafter as OH \dagger). However, current work³⁶ at pressures approaching atmospheric where the OH \dagger emission is strongly quenched also shows the 551.4- and 572.9-nm bands of glyoxal phosphorescence. The observation¹² of glyoxal as a minor product in the low-pressure *cis*-2-

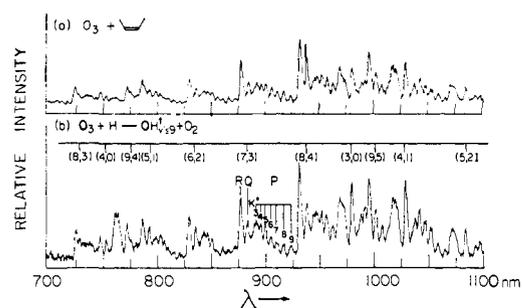
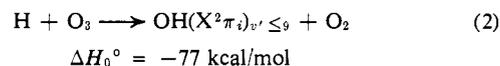


Figure 3. Comparison of the chemiluminescent emission (700–1100 nm) from the ozone-*cis*-2-butene reaction to the OH Meinel bands from the H + O₃ reaction: (i) total pressure 3.2 Torr, spectral slit width 1.2 nm; (ii) total pressure 1.02 Torr, spectral slit width 0.72 nm.

butene reaction with 2% O₃/O₂ further supports this assignment.

The broad peak at approximately 517 nm from the reaction of 2% O₃/O₂ with isobutene (Figure 2iv) is identical with that from the 2-methyl-2-butene and 2,3-dimethyl-2-butene reactions at this spectral resolution. These spectra were compared with the phosphorescence of glyoxal, methylglyoxal,³⁷ and biacetyl. Glyoxal and biacetyl, whose emission spectra were recorded with the same detection system, were eliminated as the emitting species. However, a phosphorescence spectrum of methylglyoxal furnished by Yardley and coworkers³⁷ was in good agreement and hence it is believed that this is the emitting species. The chemiluminescence at $\lambda > 440$ nm (Figure 2iii) may be the sum of formaldehyde fluorescence and methylglyoxal fluorescence.³⁷

The chemiluminescent emission spectrum from the *cis*-2-butene-ozone reaction in the region $700 < \lambda < 1100$ nm is compared in Figure 3 to that from the H + O₃ reaction under similar conditions of temperature and pressure. Reaction 2 is known^{38, 39} to produce the Meinel bands²⁹ of vibrationally excited OH \dagger (v' \leq 9), with v' = 9 corresponding to the exothermicity of the reaction



Both reactions have virtually identical vibrational distributions especially in that emission from levels v' > 9 is not observed. In addition, the rotational distributions are similar, further confirming H atoms as the precursors of the OH \dagger chemiluminescence in ozone-olefin reactions.¹¹

Secondary reactions of the major products cannot be responsible for the Meinel band chemiluminescence since only acetaldehyde⁴⁰ gives this emission on reaction with O₃ and the intensity in this case is at least a factor of 10 less than that observed in the *cis*-2-butene-ozone reaction.

To determine whether oxygen was involved in the chemiluminescent processes, spectra from the reactions

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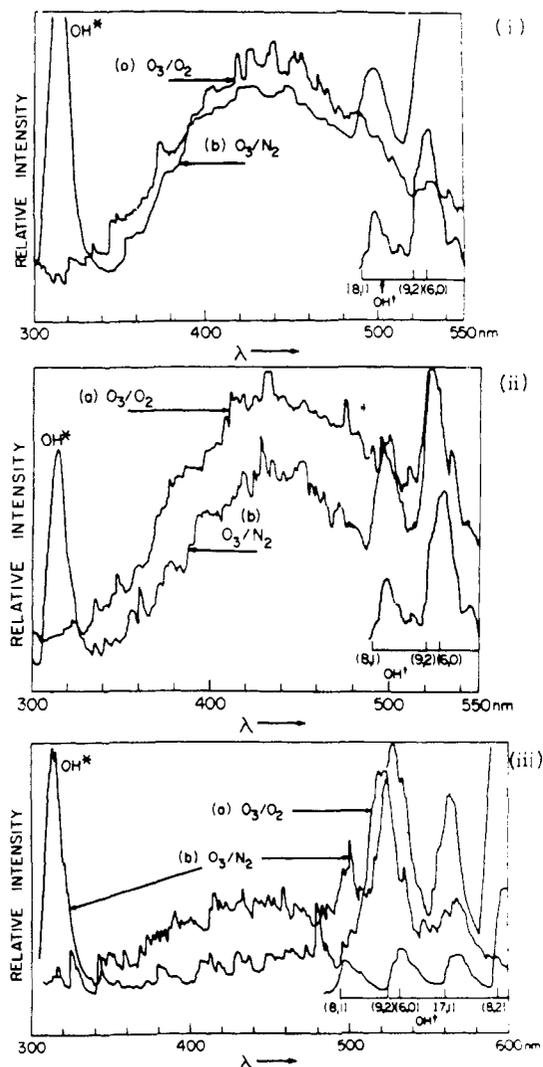


Figure 4. Chemiluminescent emission spectra (300–550 nm) from the reactions of 2% O₃ in (a) O₂ and (b) N₂ with: (i) ethylene, total pressure 1.79 Torr, spectral slit width 9.0 nm; (ii) *cis*-2-butene, total pressure 1.58 Torr, spectral slit width 7.4 nm; (iii) isobutene, total pressure 1.60 Torr, spectral slit width 7.4 nm.

of ozone with ethylene, *cis*-2-butene, and isobutene were recorded first in N₂ and then in O₂ as diluent. Use of He rather than N₂ caused no detectable change in the spectra. Figure 4 shows that the HCHO(¹A' → ¹A₁) fluorescence is unaffected by the removal of O₂. However, the Meinel bands appeared to increase in intensity and the (0,0) band of electronically excited OH(A²Σ⁺ → X²Π_i) (hereafter referred to as OH*) was observed at 306.4 nm (the (1,0) band at 281.1 nm was not detected). While the intensity of OH* in the presence of O₂ was not sufficient to be recorded using a monochromator, a signal was observed using a 317 ± 6 nm interference filter in the *cis*-2-butene and isobutene reactions.

Because of the increased intensity of the OH† Meinel bands in N₂, it could not be ascertained whether the 517- and 520-nm peaks observed in the isobutene and *cis*-2-butene reactions in O₂ were still present. Therefore, in order to eliminate the OH† emission, the spectra from the reactions of the corresponding perdeuterated olefins with O₃/O₂ and O₃/N₂ were recorded, as shown in Figure 5. As expected, no OD† emission was ob-

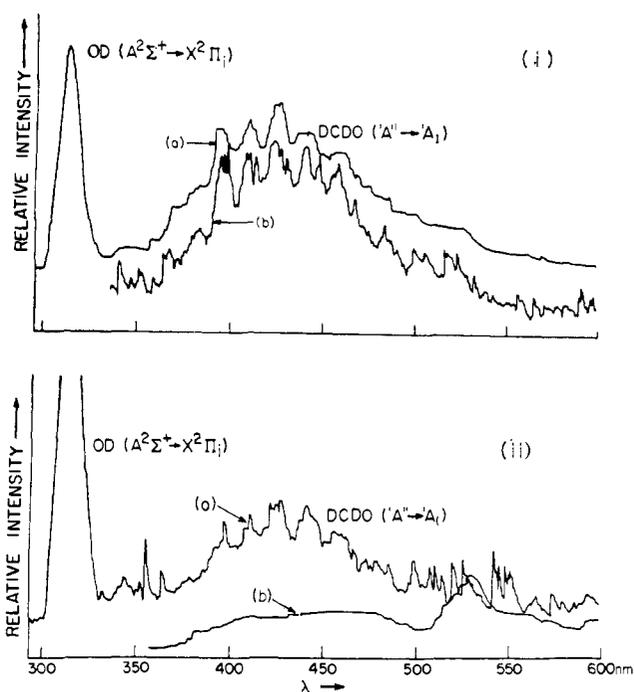


Figure 5. Chemiluminescent emission spectra (300–600 nm) from the reactions of 2% O₃ in (a) N₂ and (b) O₂ with: (i) 2-butene-d₈, total pressure 1.72 Torr, spectral slit width 9.0 nm; (ii) isobutene-d₈, total pressure 1.93 Torr, spectral slit width 9.0 nm.

served up to 700 nm. This was confirmed by the lack of OD† emission from the D + O₃ reaction in the same system. It appears that O₂ is necessary for production of the 517-nm peak tentatively identified as methylglyoxal phosphorescence in the isobutene-ozone reaction. However, the experiments with the 2-butene-d₈ were inconclusive since the glyoxal-d₂ phosphorescence was reduced by more than a factor of 2.5 even in O₂, suggesting a kinetic isotope effect.⁴¹

Table I summarizes the emitting species identified from the chemiluminescent emission spectra of the

Table I. Summary of the Chemiluminescing Species (200 < λ < 1100 nm) Identified in Ozone-Olefin Reactions in the Presence and Absence of Oxygen^a

Olefin	Carrier gas	Chemiluminescing species			
		OH†	OH*	HCHO* (CHO) ₂ *	CH ₃ CO-CHO* ^b
Ethylene	O ₂	+		+	
	N ₂	+		+	
<i>cis</i> -2-Butene	O ₂	+	+	+	+
	N ₂	+	+	+	?
<i>trans</i> -2-Butene	O ₂	+		+	+
	O ₂	+		+	
Propylene	O ₂	+		+	c
1-Butene	O ₂	+		+	c
Isobutene	O ₂	+	+	+	+
	N ₂	+	+	+	
2-Methyl-2-butene	O ₂	+		+	+
2,3-Dimethyl-2-butene	O ₂	+		+	+

^a + denotes positive identification of emitting species; a blank indicates that chemiluminescence from this species was not observed. ^b Tentative identification; see text. ^c Not studied at high resolution.

(41) R. Livingston in "Techniques of Organic Chemistry," 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, Chapter II.

ozone-olefin reactions in the wavelength region 200 to 1100 nm.

Kinetics of Light Emission. (a) Intensity of Light Emission as a Function of Reactant Concentration. The dependence of each of the emission intensities on olefin and ozone concentration was investigated under pseudo-first-order conditions. Reaction orders were determined from least-squares analyses of the slopes of log-log plots of emission intensity *vs.* reactant concentration. Table II shows that the emission intensities were

Table II. Reaction Orders of Emitting Species in Ozone and Olefin in the Presence and Absence of Oxygen, Respectively^a

Olefin	Carrier gas	Emitting species		
		HCHO*	OH†	517- or 520-nm peak
Ozone				
Ethylene	O ₂	1.04 ± 0.04	1.04 ± 0.03	
	N ₂	1.09 ± 0.07	1.03 ± 0.05	
Isobutene	O ₂	1.06 ± 0.04	0.93 ± 0.05	0.39 ± 0.02 ^b
	N ₂	0.99 ± 0.04	1.00 ± 0.01	
<i>cis</i> -2-Butene	O ₂	0.95 ± 0.03	1.14 ± 0.01	0.97 ± 0.02 ^c
	N ₂	0.89 ± 0.03	1.01 ± 0.03	
Olefin				
Isobutene	O ₂	1.06 ± 0.05	0.97 ± 0.04	1.00 ± 0.05 ^b
<i>cis</i> -2-Butene	O ₂	0.96 ± 0.06	1.12 ± 0.11	1.10 ± 0.09 ^c

^a Errors given are least-squares standard deviations. ^b Tentatively identified as methylglyoxal phosphorescence. ^c Assigned as glyoxal phosphorescence, (CHO)₂(³A_u → ¹A_g).

first order in each reactant, with the exception of the isobutene reaction where the order of the 517-nm peak in ozone was 0.39 ± 0.02 in O₂ as carrier gas. With N₂ as carrier gas, the light emission generally exhibited a maximum at very low olefin concentrations and then decreased with increasing olefin concentration.

(b) Decay of Light Intensity and Ozone. For ethylene, *cis*-2-butene, and isobutene, the intensities of each of the chemiluminescent emissions and the O₃ concentration were determined as a function of time with O₂ or N₂ as the diluent gas over total pressures of 2–10 Torr. In order to maintain pseudo-first-order conditions, the initial olefin concentrations were a minimum of six, and typically ten, times the initial ozone concentration. Decay rates were determined from the least-squares slopes of plots of the logarithms of either emission intensity or ozone absorbance against reaction time. Typical data for the *cis*-2-butene reaction with ozone are shown in Figure 6. Similar behavior was observed for the ethylene and isobutene reactions.

Figure 6i shows that in O₂ as carrier gas the emission intensities and the ozone concentration both decay exponentially at times >0.1 sec. The ratio (decay rate of emission intensity)/(rate of ozone decay) was determined for each run from plots such as those shown. The average value of this ratio in the pressure range of 2–10 Torr was approximately 1.4 for all emissions. However, this ratio was observed to decrease with increasing oxygen or olefin concentration. For example, at 1.8 Torr total pressure, this ratio was 1.6 for formaldehyde fluorescence; on addition of O₂ to a total pressure of 9.6 Torr, this ratio fell to 1.0.

In N₂ as carrier gas, high initial light intensities occurred, followed by nonexponential decays as seen in Figure 6ii. The apparent increase in the intensity of

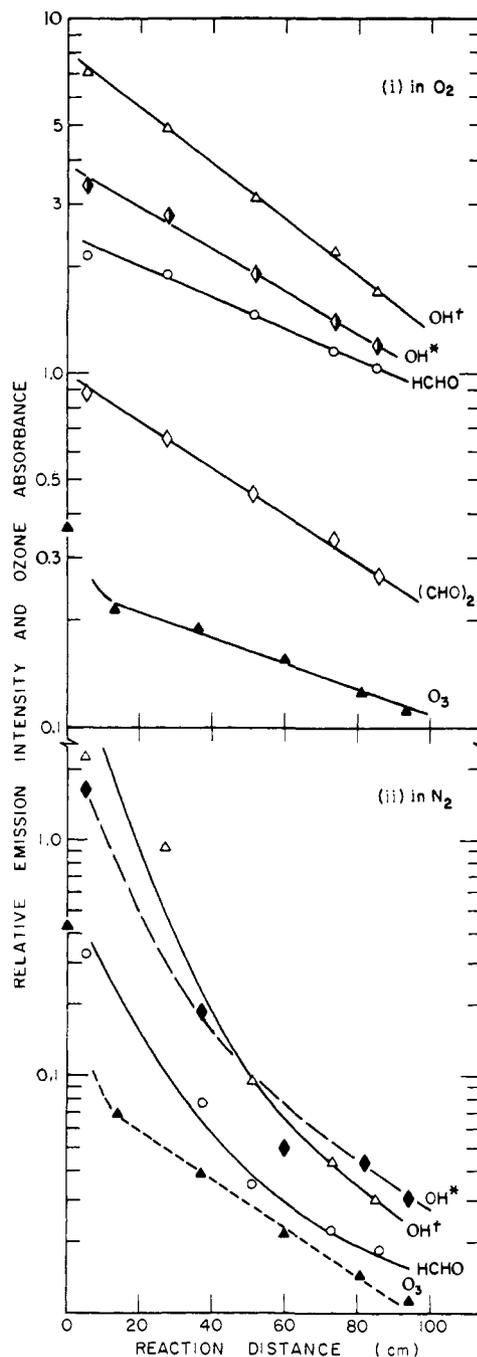


Figure 6. Semilogarithmic plots of relative emission intensities and ozone absorbance *vs.* reaction distance for the reaction of *cis*-2-butene with (i) 2% O₃/O₂ and (ii) 2% O₃/N₂. Initial flow rate of *cis*-2-butene, 16–22 μmol/sec; initial ozone flow rate 2.5 μmol/sec; total pressure 5.3–9.2 Torr; 100 cm corresponds to a reaction time of 1.3 sec.

the Meinel bands (Figure 4) on the replacement of O₂ by N₂ is thus due to the increased initial light intensity rather than to an overall increase at all reaction times. While the ozone decayed even more rapidly than in O₂ at times ≤0.1 sec., a slower exponential decay followed.

(c) Relationship of OH* and OH†. In the *cis*-2-butene reaction, the relationship of the OH* emission intensity to that of OH† in both O₂ and N₂ as diluent gas was investigated by simultaneously following both emission intensities as a function of reaction time. The least-squares slopes of the log-log plots of OH* emission intensity *vs.* OH† intensity for each run in a series of

Table III. Rate Constants for the *cis*-2-Butene and Isobutene Reactions with Ozone Under Varying Conditions of Total Pressure and Oxygen Concentration^a

Exptl conditions	<i>cis</i> -2-Butene		Isobutene	
	Total press, Torr	$10^{-4} \times k$, l. mol ⁻¹ sec ⁻¹	Total press, Torr	$10^{-4} \times k$, l. mol ⁻¹ sec ⁻¹
O ₃ /O ₂ from ozonizer used; no additional diluent added	1.8-2.1	9.2 ± 2.3	1.7-1.9	1.4 ± 0.4
O ₃ /O ₂ from ozonizer used; O ₂ added as diluent	3.9-4.0	7.3 ± 2.0	3.9-4.2	0.82 ± 0.28
	4.5-5.9	6.7 ± 1.8	6.4-6.6	0.63 ± 0.23
	7.3-7.4	7.1 ± 2.0	9.3-9.7	0.54 ± 0.23
	8.9-9.6	6.3 ± 1.9		
O ₃ /N ₂ from silica gel trap used; O ₂ added as diluent	5.5-5.6	6.5 ± 1.9	4.4-4.5	0.84 ± 0.29
	8.9-9.1	6.0 ± 1.9		
O ₃ /N ₂ from silica gel trap used; no additional diluent added	1.9-2.0	17 ± 5	1.9-2.0	4.2 ± 1.2
O ₃ /N ₂ from silica gel trap used; N ₂ added as diluent	5.4-6.1	13 ± 4	4.2-4.5	3.8 ± 1.3
	9.1-10.0	16 ± 5	6.8-7.1	3.0 ± 1.0
			9.6-9.9	3.7 ± 1.1

^a Error limits shown are the estimated overall errors which include both the precision of the data as well as experimental errors.

Table IV. Comparison of the Rate Constants Obtained in This Work with Literature Room-Temperature Values

Olefin	Total press, Torr	Concn, ppm ^a		Rate constant × 10 ⁻³ , ^b l. mol ⁻¹ sec ⁻¹	Ref
		Ozone	Olefin		
Ethylene	760	0.3-0.7	5-55	0.93 ± 0.09	46
	Atm	0.5-3	4-8	1.8 ^c	45
	Atm	~20	~20	0.8	6
	150-650	<i>d</i>	<i>d</i>	2.1 ± 0.8	43
	100 ± 20	~2500	~20,000	1.6 (O ₂) ^e	8
				1.2 (N ₂) ^e	
				2.4 (O ₂) ^e	7
<i>cis</i> -2-Butene	110-135	~3000	~48,000	1 ± 1 (O ₂)	This work
	2-10	~50	~400	5 ± 2 (N ₂)	
	Atm	0.35-0.9	1-2	85	
	Atm	<i>f</i>	<i>f</i>	90 (N ₂)	10
	Atm	~4-8	~5-11	200	45
	100 ± 20	~2500	~20,000	29	6
				16.6 (O ₂) ^e	8
Isobutene	50-60	~1200	~24,000	11.5 (N ₂) ^e	7
	2-10	~50	~400	17.5 (O ₂) ^e	This work
				60-92 (O ₂)	
	Atm	~0.5-1	~1-3	130-170 (N ₂)	44
	Atm	<i>f</i>	<i>f</i>	8.8 ± 2.2	6
	Atm	<i>f</i>	<i>f</i>	3.7	45
	100 ± 20	~2500	~20,000	14 ± 2	8
			4.9 (O ₂) ^e		
Isobutene	110-135	~3000	~48,000	5.8 (N ₂) ^e	7
	2-10	~50	~400	4.8 (O ₂) ^e	This work
				5-14 (O ₂)	
				30-42 (N ₂)	

^a 1 ppm = 4.1 × 10⁻⁸ mol l⁻¹ = 7.6 × 10⁻⁴ Torr. ^b Unless otherwise specified, experiments were carried out in air. ^c Dynamic system, $k = 1.6 \pm 0.2 \times 10^3$ l. mol⁻¹ sec⁻¹. Static system, $k = 2.0 \times 10^3$ l. mol⁻¹ sec⁻¹. ^d Ethylene and ozone reactant concentrations varied over the range 185-4500 ppm. ^e Relative rates measured; normalized to $k = 6.12 \times 10^3$ l. mol⁻¹ sec⁻¹ for 1-hexene.⁴⁶ ^f Not reported.

experiments at varying total pressure and reactant concentrations averaged 0.97 ± 0.04 in the presence of O₂ and 0.91 ± 0.06 in N₂.

Similar investigations were carried out for the reactions of ethylene and isobutene with O₃ in N₂ as carrier gas. While the data were more scattered than that for the *cis*-2-butene reaction, the average slopes of the log-log plots were 1.09 ± 0.08 and 1.35 ± 0.11 , respectively.

Kinetics of Ozone Decay. With olefin at least a factor of 6 in excess over O₃, the rate of decay of ozone was measured under similar conditions as those used for recording the chemiluminescent emission spectra. Varying flows of nitrogen or oxygen were then added to a maximum total pressure of 10 Torr, and the rate of

ozone decay was measured at each pressure. The results of these experiments for the *cis*-2-butene and isobutene reactions are given in Table III.

Although the overall uncertainties in the rate constants measured are approximately ±30%, Table III shows that the measured rates are larger by a factor of 2-5 in the presence of N₂ as compared to those measured in O₂ and decrease slightly with increasing O₂ concentration.

Under these experimental conditions, the rate constant for the ethylene-ozone reaction was estimated to be $1 \pm 1 \times 10^3$ l. mol⁻¹ sec⁻¹ in O₂ and $5 \pm 2 \times 10^3$ l. mol⁻¹ sec⁻¹ in N₂.

The rate constants from this work are compared in Table IV with literature room-temperature

values.^{6-10, 42-46} The values in O₂ are seen to be in general agreement with the literature, indicating no significant change in the kinetics with total pressure.

Stable Product Analysis. The major stable products identified by gc from the *cis*-2-butene-ozone reaction at 2 to 10 Torr were acetaldehyde and 2-butanone in both O₂ and N₂ as diluents and methyl vinyl ketone in O₂ only. Two unidentified products were also observed in O₂. The acetaldehyde yield increased relative to that of the 2-butanone with increasing pressures of O₂. These product identifications are supported by the observations of mass peaks corresponding to all of these products in earlier photoionization mass spectrometer studies¹² of this reaction.

Absolute Rates of Light Emission. The total rate of light emission from each emitting species in the ethylene and *cis*-2-butene reactions with 2% O₃/O₂ is given in Table V; that for OH† refers to light emission from the (9,3) transition only.

Table V. Absolute Rates of Light Emission^a (l. mol⁻¹ sec⁻¹) for Each Emitting Species in the Reactions of 2% O₃/O₂ with Ethylene and *cis*-2-Butene at a Total Pressure of 4.6 Torr

Olefin	Emitting species		
	HCHO*	OH†	(CHO) ₂ *
Ethylene	1 × 10 ⁻⁴	1 × 10 ⁻⁴	
<i>cis</i> -2-Butene	7 × 10 ⁻³	5 × 10 ⁻³	0.7

^a For HCHO* and (CHO)₂*, the total rate of light emission, $k_{\text{X(TOT)}}$, calculated as described in the text, is given. For OH†, the rate of light emission is that in the (9,3) transition only, which is expected to be a function of the reactant concentrations (see Discussion).

Temperature Rise Studies. In order to investigate the self-heating of the gases^{7,8,42} during these exothermic reactions, the temperature rise was recorded at each of the five thermistors for the reaction of a series of olefins with O₃/O₂ or O₃/N₂. In the reaction with O₃/O₂, the magnitude of the maximum temperature rise increased in the order ethylene < propylene ~ 1-butene ~ isobutene < *cis*-2-butene < 2-methyl-2-butene ~ 2,3-dimethyl-2-butene which is also the order in which the rate constants increase.^{6-10, 42-46} Furthermore, the temperature rise increased with flow rate of either ozone or olefin and decreased with increasing reaction time, showing that the heat release is related to the amount of reaction occurring.

The reactions of ethylene, *cis*-2-butene, and isobutene with O₃/N₂ showed a greater temperature rise than the corresponding reactions in oxygen, although the increase in temperature was confined to shorter reaction times in agreement with the above observations. The maximum temperature rise observed was ≤ 7°, which would not have a significant effect on the rate constants^{9,43,45} measured here.

(42) H. E. Smith and R. H. Eastman, *J. Amer. Chem. Soc.*, **83**, 4274 (1961).

(43) R. D. Cadle and C. Schadt, *J. Amer. Chem. Soc.*, **74**, 6002 (1952).

(44) E. A. Schuck, G. J. Doyle, and N. Endow, Air Pollution Foundation, Report No. 31, San Marino, Calif., 1960.

(45) J. J. Bufalini and A. P. Altschuller, *Can. J. Chem.*, **43**, 2243 (1965).

(46) D. H. Stedman, C. H. Wu, and H. Niki, *J. Phys. Chem.*, **77**, 2511 (1973).

Discussion

***cis*-2-Butene Reaction.** The mechanism of ozone-olefin reactions proposed by O'Neal and Blumstein²³ is applied to the ozone-*cis*-2-butene reaction in Scheme I. Included are recent modifications⁴⁷ to the original scheme relevant to our studies.

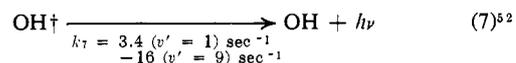
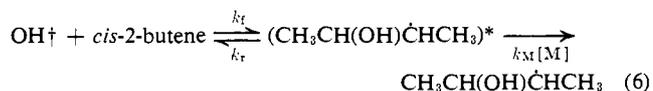
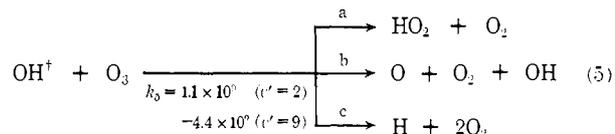
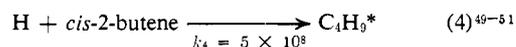
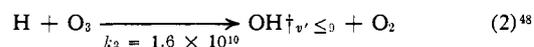
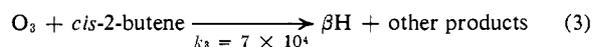
At a total pressure of ~2 Torr, it is anticipated that (1) α-hydrogen abstraction should occur at a rate approximately 2.5 faster than the Criegee fragmentation assuming some stabilization of the Criegee biradical by polarization of charge, (2) collisional stabilization of the excited α-keto hydroperoxide (reaction a) and decomposition (reactions b to e) should be competitive such that both the α-keto hydroperoxide and the intermediates and stable products predicted by reactions b to e should be observed, and (3) β-hydrogen abstraction of the peroxy biradical will occur at a rate slower by a factor of ~8 than the α-hydrogen abstraction path, leading to the formation of an excited 1,2-dioxetane.

One can now compare these predictions to the experimental data for the *cis*-2-butene-ozone reaction obtained in this and earlier studies.^{11,12}

(a) OH† Meinel Band Emission. Application of simple unimolecular (RRK) theory to the thermochemistry predicted by O'Neal indicates that due to the ~140 kcal/mol released in the rearrangement of the biradical to acetic acid (step f) its decomposition (step f') should occur at a rate several orders of magnitude greater than collisional quenching at 2 Torr.⁴⁷ It is also possible⁴⁷ that the acetic acid formed in step b may contain enough of the reaction exothermicity to decompose in an analogous manner. Since the observed yield of CH₃CHO at 2 Torr is ~1,¹² but CH₃COOH was not observed, the yield of H atoms may approach unity under our experimental conditions.

The dominant loss process for H atoms formed in step f' and possibly b' under these conditions¹² must be the well-known chemiluminescent reaction 2^{29,38,39} with O₃.

A simplified scheme for the formation and loss of OH† is then given by



(47) H. E. O'Neal, personal communication, 1973.

(48) L. F. Phillips and H. I. Schiff, *J. Chem. Phys.*, **37**, 1233 (1962).

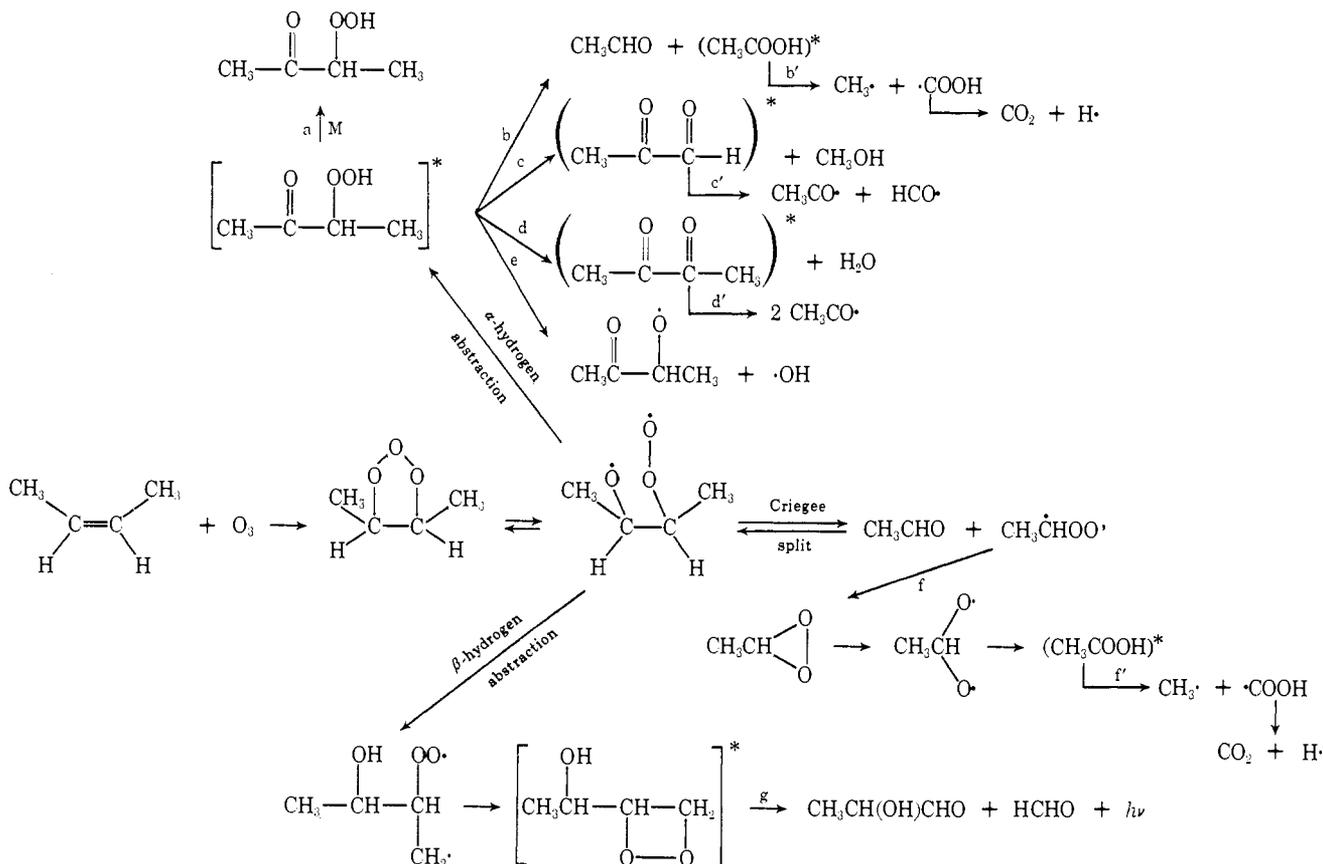
(49) E. E. Daby and H. Niki, *J. Chem. Phys.*, **51**, 1225 (1969).

(50) J. A. Cowfer, D. G. Keil, J. V. Michael, and C. Yeh, *J. Phys. Chem.*, **75**, 1584 (1971).

(51) E. E. Daby, H. Niki, and B. Weinstock, *J. Phys. Chem.*, **75**, 1601 (1971).

(52) R. N. Coltharp, S. D. Worley, and A. E. Potter, *Appl. Opt.*, **10**, 1786 (1971).

Scheme I



where the rate constants are in liters per mole second units unless otherwise specified and β is the fraction of reaction 3 giving H atoms. Hence

$$[\text{OH}\ddagger] = \frac{\beta k_3 k_2 [\text{O}_3]^2 [\text{olefin}]}{\{k_3[\text{O}_3] + k_6[\text{olefin}] + k_7\} \{k_2[\text{O}_3] + k_4[\text{olefin}]\}} \quad (\text{III})$$

where $k_6 = k_1 k_M [\text{M}] / (k_7 + k_M [\text{M}])$, k_1 , k_7 , and k_M are the rate constants for the steps outlined in reaction 6 above, and in all cases $k_7 \ll k_5 [\text{O}_3]$.

The overall rate constant for reaction 6 for ground state $\text{OH}(v' = 0)$ with *cis*-2-butene at a total pressure of ~ 1 Torr is 3.7×10^{10} l. mol⁻¹ sec⁻¹.^{53,54} The observed⁵³ enhancement of the OH-propylene adduct mass peaks as the total pressure was increased from 1 to 4 Torr suggests that at least for propylene the adduct can also decompose, one path possibly being that back to the reactants. Because of the high room-temperature rate constant for the reaction of $\text{OH}(v' = 0)$ with *cis*-2-butene, the activation energy must be low and hence an increase in the vibrational energy of the reacting OH radical is anticipated to substantially increase the rate of decomposition of the adduct, k_7 , while not significantly affecting the forward rate, k_1 . Hence the overall rate constant, k_6 , is expected to decrease as the vibrational energy content of the OH radical increases.

An estimate of k_6 for vibrationally excited $\text{OH}\ddagger$ can be obtained as follows; assuming an activation energy for the forward reaction of ~ 1 kcal/mol and $\Delta H_f^\circ =$

-28 kcal/mol⁵⁵ for the adduct, $\text{CH}_3\text{CH}(\text{OH})\dot{\text{C}}\text{HCH}_3$, then from unimolecular theory,⁵⁷ $k_7 \sim 2 \times 10^8$ sec⁻¹ ($v' = 7-8$). Assuming $k_M [\text{M}] = 2 \times 10^7$ sec⁻¹, then $k_6 \sim 4 \times 10^9$ l. mol⁻¹ sec⁻¹,⁵⁸ which, though very approximate, can now be applied to the kinetics of $\text{OH}\ddagger$ formation.

In the experiments to determine the reaction order of $\text{OH}\ddagger$ with respect to olefin, $[\text{O}_3] \geq 2 [\text{olefin}]$, thus $k_2 [\text{O}_3] \gg k_4 [\text{olefin}]$ and hence eq III simplifies to

$$[\text{OH}\ddagger] = \frac{\beta k_3 [\text{O}_3] [\text{olefin}]}{k_3 [\text{O}_3] + k_6 [\text{olefin}]} \quad (\text{IV})$$

Using $k_6 \approx 4 \times 10^9$ l. mol⁻¹ sec⁻¹, $k_3 [\text{O}_3] > k_6 [\text{olefin}]$, and hence $[\text{OH}\ddagger] \propto [\text{olefin}]$, consistent with Table II.

Similarly, when studying the dependence of $\text{OH}\ddagger$ on $[\text{O}_3]$, $[\text{olefin}] \geq 10 [\text{O}_3]$. Then $k_2 [\text{O}_3] > k_4 [\text{olefin}]$ and $k_6 [\text{olefin}] > k_3 [\text{O}_3]$. Hence $[\text{OH}\ddagger] \propto [\text{O}_3]$, as observed.

In order to calculate the total rate of light emission from all vibrational levels of $\text{OH}\ddagger$, and hence the yield of $\text{OH}\ddagger$, the vibrational distribution must be known. It was not possible in these experiments to determine

(55) ΔH_f° was calculated using Benson's group additivity method.⁵⁶

(56) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(57) $k_7 = A((E - E_0)/E)^{s-1}$ where $A \approx 10^{13}$ sec⁻¹, $(s - 1)_{\text{eff}} \approx 24$, $E_0 = 37$ kcal/mol, and $E = E_{\text{OH}\ddagger} + 36$ kcal/mol, where $E_{\text{OH}\ddagger}$ is the vibrational energy content of the $\text{OH}\ddagger$ radical.

(58) It is likely that diatomics (O_2 or N_2) will not stabilize the excited adduct molecule with unit efficiency,⁵⁹ hence decreasing the calculated value of k_6 . The existence of alternate decomposition paths for the excited adduct will increase k_6 . Unfortunately, at the present time, no information is available on the fate of the excited adduct.

(59) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, New York, N. Y., 1972, and references therein.

(53) E. D. Morris, Jr., D. H. Stedman, and H. Niki, *J. Amer. Chem. Soc.*, **93**, 3570 (1971).

(54) E. D. Morris, Jr., and H. Niki, *J. Phys. Chem.*, **75**, 3640 (1971).

this distribution and hence only a crude estimate of the total rate of light emission can be obtained. Garvin, *et al.*,⁶⁰ have shown that at 4.2 Torr total pressure in O₂ and H₂ the vibrational distribution of OH† from reaction 2 is Boltzmann and corresponds to a vibrational temperature of 9250°K. However, in the presence of olefin with which OH† reacts, the lower vibrational levels may be preferentially removed leading to a higher effective vibrational temperature. Calculating k_6 as a function of OH† vibrational energy content as described above, and modifying the Boltzmann distribution found by Garvin, *et al.*,⁶⁰ for the increased removal of OH† in lower vibrational energy levels, the H atom yield per molecule of reactant consumed is estimated to be approximately 1 within order of magnitude error limits, under these experimental conditions.

(b) HCHO(¹A' → ¹A₁). The experimentally observed first-order kinetics of formaldehyde fluorescence are consistent with the production of electronically excited HCHO from the decomposition of an excited 1,2-dioxetane, step g of Scheme I.

Using $k_3 = 7 \times 10^4$ l. mol⁻¹ sec⁻¹ for the *cis*-2-butene-O₃ reaction at 4.6 Torr (Table III) and $k_{\text{X(TOT)}} = 7 \times 10^{-3}$ l. mol⁻¹ sec⁻¹ for formaldehyde fluorescence (Table V), the number of light quanta emitted from electronically excited formaldehyde per molecule of reactant consumed is $\sim 1 \times 10^{-7}$. These low values are consistent with the concerted process (step g) since both the decomposition of 1,2-dioxetanes to produce the first excited singlet state⁶¹ and HCHO fluorescent emission are inefficient processes.

Other sources of HCHO(¹A'') such as

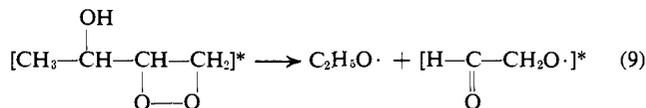


cannot be definitely excluded, particularly at the low pressures and relatively high OH concentrations present under these conditions. Reaction 8 is thought to be responsible for the weak formaldehyde fluorescence observed as a general phenomenon in the low-temperature gas-phase oxidation of organic compounds.^{62,63} Although OH radicals are known to be present in the *cis*-2-butene-ozone reaction, no CH₃O radicals were detected in the PMS studies.¹² This does not preclude the production of CH₃O since if its loss is by reaction with olefin with a rate constant of 10⁷-10⁸ l. mol⁻¹ sec⁻¹,⁶⁴ then its steady state concentration would have been below the detection limits.

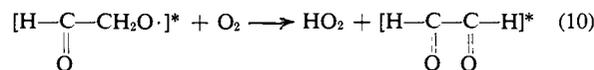
(c) Glyoxal Phosphorescence. Although glyoxal phosphorescence has been observed from the recombination of HCO radicals,⁶⁵ this seems highly unlikely in the presence of excess O₂ which reacts rapidly with HCO.⁶⁶ In addition, this recombination, which is second order in HCO, would not be kinetically consistent with both the first-order dependence of light

intensity on reactants and with the direct production of HCO from the ozone-olefin adduct *via* steps c and c'.

The observation of glyoxal phosphorescence in the presence of 2 Torr of O₂, and indeed at higher pressures,³⁶ is rather surprising. One energetically possible route involves an alternate mode of decomposition of the 1,2-dioxetane formed by β-H abstraction



followed by reaction of the excited alkoxy radical with O₂.



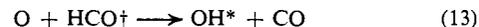
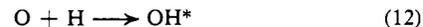
While (9) and (10) are speculative, it appears that the partitioning of energy in these reactions may result in sufficient energy input to the glyoxal to cause electronic excitation. Furthermore, this mechanism is consistent with the observed kinetic isotope effect (Figure 5), the first-order kinetics of the light emission, and the observation of glyoxal phosphorescence at pressures approaching atmospheric.³⁶

(d) Electronically Excited OH. OH* has been observed⁶⁷ in the H + O₃ reaction as a product of energy pooling.



However, the width of the (0,0) band envelope of OH(A²Σ⁺ → X²π_i) from reaction 11 was greater than that from the ozone-olefin reactions. In addition, the observed first-order dependence of electronically excited OH* on the vibrationally excited OH† radical rules out reaction 11 as the source of OH*.

One possible source of electronically excited OH* radicals in this system involves O atom reactions. Thus, Becker, Kley, and Norstrom⁶⁸ in their studies of OH* chemiluminescence in the O-C₂H₄ flame observed rotationally cool emission from OH*. The reactions of an O atom with either an H atom or an excited HCO radical to produce OH* were suggested.



A mode of production of O atoms in the ozone-olefin system is the decomposition of O₃ by OH† radicals with $v' \geq 3$.⁶⁹



The OH* emission intensity is strongest for the ethylene reaction, relative to the HCHO* and OH† emissions, supporting an O atom precursor as the relative rates of reaction of O(³P) with ethylene, isobutene, and *cis*-2-butene are 1:25:24.⁷⁰

(e) Effects of Oxygen. In nitrogen as diluent, the initial steps of the ozone-*cis*-2-butene reaction as outlined above must remain the same. However, the secondary reactions of radicals which react rapidly with O₂ will be strongly dependent on its presence. For

(67) H. P. Broida, *J. Chem. Phys.*, **36**, 444 (1962).

(68) K. H. Becker, D. Kley, and R. J. Norstrom, 12th International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1969, p 405, and references therein.

(69) W. B. DeMore, *J. Chem. Phys.*, **46**, 1813 (1967).

(70) R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963), and references therein.

(60) D. Garvin, H. P. Broida, and H. J. Kostkowski, *J. Chem. Phys.*, **32**, 880 (1960).

(61) N. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2887 (1972).

(62) J. H. Knox in "Photochemistry and Reaction Kinetics," P. G. Ashmore, F. S. Dainton, and T. M. Sugden, Ed., Cambridge University Press, London, 1967, pp 250-286.

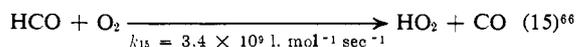
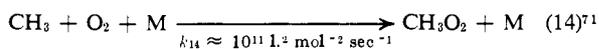
(63) V. Ya. Shlyapintokh, *et al.*, "Chemiluminescence Techniques in Chemical Reactions," N. M. Emanuel, Ed., translated from Russian, Consultants Bureau, New York, N. Y., 1968, and references therein.

(64) K. L. Demerjian, J. A. Kerr, and J. G. Calvert, *Advan. Environ. Sci. Technol.*, **4**, 1 (1974).

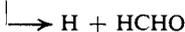
(65) D. B. Hartley, *Chem. Commun.*, 1281 (1967).

(66) N. Washida, R. I. Martinez, and K. D. Bayes, *Z. Naturforsch. A*, **29**, 251 (1974).

example, CH_3 and HCO which react with O_2 under these conditions will, in N_2 as diluent, react with O_3 .



The products of their reactions with O_3 are likely more reactive than the CH_3O_2 and HO_2 produced in reactions 14 and 15, respectively. For example, if excited CH_3O and HCO are formed, H atoms could be produced.^{64,72}



Therefore in the absence of O_2 one anticipates increased rates of O_3 decay due to secondary radical attack and possibly increased Meinel band emission intensity if H atoms are indeed produced in reactions 16 and 17.

This is in qualitative agreement with our experimental observations that: (1) the measured rate constant for O_3 decay in N_2 as diluent is larger than in O_2 , (2) a rapid loss of O_3 occurs in the first ≤ 0.1 sec which is accompanied by intense light emission, particularly of OH^\dagger and OH^* , and (3) a measurable temperature rise occurs, particularly in the vicinity of the mixing jet.

The nonexponential decay of each of the light emissions in N_2 as diluent may then be due to a change in the relative rates of competing reactions such as (5) and (6) over the time period studied, since reaction 6 is a termination step in the chain formed by reactions 2 and 5c. Similar processes must also occur to some extent in 2 Torr of O_2 since the emitting species generally show first-order behavior on O_3 (Table II) and yet the rate of decay of light intensity is generally greater than the rate of O_3 decay. Increasing the pressures of O_2 up to 10 Torr appears to further quench one or more radical precursors to the chemiluminescence since the ratio (rate of decay of light intensity)/(rate of O_3 decay) approaches unity at ~ 10 Torr of O_2 .

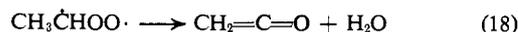
(f) **Intermediates and Products.** Many of the intermediates and stable products predicted by Scheme I were observed either by photoionization mass spectrometry,¹² gc, or both. Thus, HCO and HO_2 , possibly from reactions c, c', and 15,⁶⁶ were observed.¹² In addition, HCHO , CH_3OH , CH_3CHO , CH_2CO , and an ozone-olefin adduct believed to be the α -keto hydroperoxide, $\text{CH}_3\text{CH}(\text{OOH})\text{COCH}_3$, were detected.¹²

On the other hand, 2-hydroxypropanal which should have been formed in equal quantities to HCHO (step g) was not seen. In addition, while CH_3O_2 and $\text{C}_2\text{H}_5\text{O}$ radicals were observed,¹² their nonsteady state behavior suggested that they were not primary reaction products but were formed in the mass spectrometer. Hence, their production is uncertain, although reactions 14 and 9 may be possible contributors.

In the PMS studies, ketene was also observed as a major product.¹² Its formation can be rationalized in terms of a "classical" rearrangement of the Criegee zwitterion as suggested by Scott, Hanst, and co-workers.^{5,6,72a}

(71) N. Basco, D. G. L. James, and F. C. James, *Int. J. Chem. Kinet.*, **4**, 129 (1972).

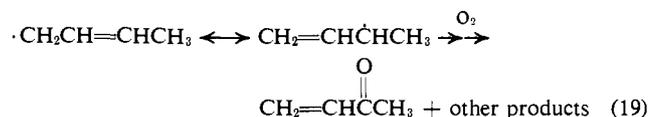
(72) P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. React. Kinet.*, **4**, 63 (1967).



Significant quantities of methyl vinyl ketone and 2-butanone were observed by gc and peaks corresponding to these products were observed by photoionization mass spectrometry.¹² The identification of 2-butanone by gc provides the best explanation of the m/e 72 peak although it might contain some contribution due to methylglyoxal (reaction c).

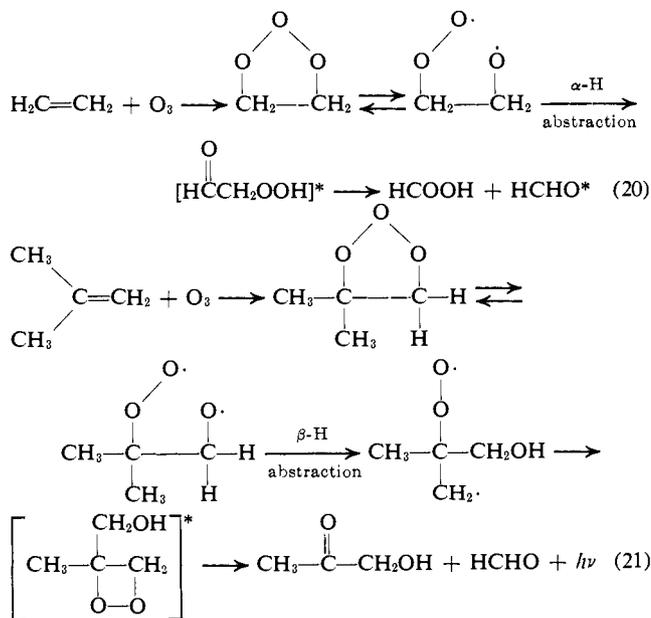
The 2-butanone may be due to the reaction of OH with *cis*-2-butene. The mechanism of this reaction is not clear, although an OH -olefin adduct has been observed mass spectrometrically.⁵³ Preliminary studies⁷³ of the OH -*cis*-2-butene reaction in the presence and absence of oxygen indicate that both 2-butanone and acetaldehyde are formed in significant yields, with the ratio of acetaldehyde to 2-butanone increasing on the addition of oxygen, consistent with our observations.

Radical abstraction from *cis*-2-butene will form the radical $\cdot\text{CH}_2\text{CH}=\text{CHCH}_3$. It was suggested in earlier studies¹² that in the presence of O_2 this radical might subsequently react with O_2 to form methyl vinyl ketone and hence a peak at m/e 70.



Formation of methyl vinyl ketone by reaction 19 is supported by the fact that it was below the gc detection limit in the *cis*-2-butene- O_3/N_2 system but was observed in O_2 as diluent.

Ethylene and Isobutene Reactions. Formaldehyde fluorescence and OH^\dagger Meinel band emissions are common to all three olefin reactions studied. Possible routes to the formation of electronically excited formaldehyde which are consistent with the observed first-order kinetics involve α -H abstraction and β -H abstraction, respectively.^{23,47}

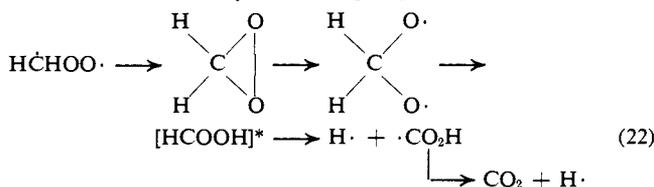


As in the *cis*-2-butene-ozone reaction, efficient

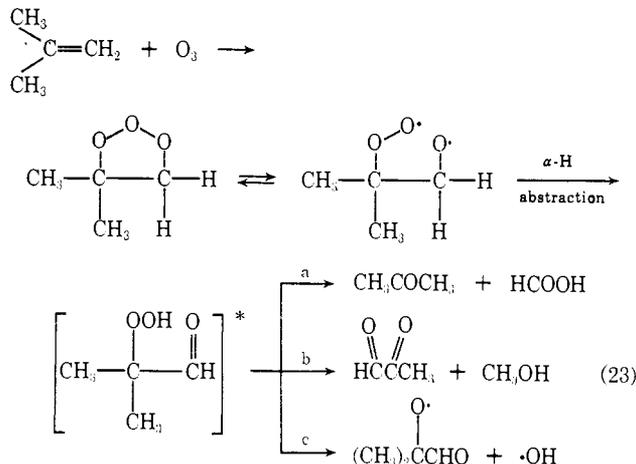
(72a) NOTE ADDED IN PROOF. Reaction 18 may proceed via the excited CH_3COOH formed from the rearrangement of the Criegee biradical $\text{CH}_3\dot{\text{C}}\text{HOO} \cdot$ since the pyrolysis of CH_3COOH leads to the formation of CH_2CO and H_2O : P. G. Blake and G. E. Jackson, *J. Chem. Soc. B*, 94 (1969), and references therein.

(73) R. J. Cvetanovic, personal communication, 1973.

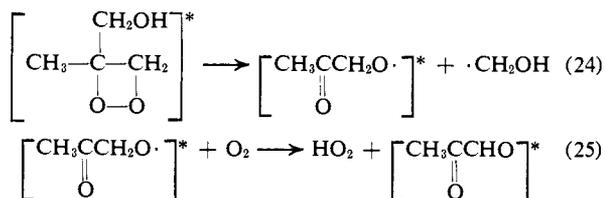
H-atom production and hence relatively strong OH† Meinel band emission are anticipated in both of these reactions at 2 Torr from the decomposition of excited HCOOH formed by the Criegee path.



While in the isobutene reaction, a proposed^{23,47} route to the formation of methylglyoxal is the α -H



abstraction, reaction 23b; the kinetics of the emission (Table II) suggest a more complex mechanism than reaction 23b. The apparent involvement of O₂ is also difficult to rationalize by this scheme, as is the observation of excited methylglyoxal from the 2-methyl-2-butene and 2,3-dimethyl-2-butene reactions. However, in the alternate mode of decomposition of the 1,2-dioxetane formed by β -hydrogen abstraction, analogous to that proposed above for the *cis*-2-butene, reactions 9 and 10 may give electronically excited methylglyoxal.

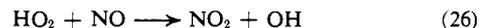


Reactions 24 and 25 would explain why O₂ is necessary to produce excited methylglyoxal. In addition, one anticipates a decreased ratio of the intensities of methylglyoxal phosphorescence to formaldehyde fluorescence in the isobutene-*d*₈ reaction, due to kinetic isotope effects,⁴¹ as is observed (Figure 5ii).

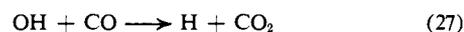
The effects of replacing the O₂ diluent by N₂ are expected to be similar to those in the *cis*-2-butene reaction, consistent with experiment.

Atmospheric Implications. In the formation of photochemical smog, the rate of oxidation of NO to NO₂ in excess of that due to O atom and O₃ reactions is currently thought⁷⁴⁻⁷⁶ to be due at least in part to the

HO₂ reaction



HO₂ may then be regenerated in a chain process involving the OH radical



Hence any reaction producing H atoms or OH in the atmosphere may contribute to the NO to NO₂ oxidation. OH has recently been detected⁷⁷ in ambient air, lending support to this postulate.

If these data can be extrapolated to atmospheric conditions (and it is not clear at the present time that this is the case), then the reaction of ozone with small olefins ($\lesssim \text{C}_5$) will be a source of H atoms and hence contribute to the NO to NO₂ conversion *via* reactions 26 to 28.

It is possible that the enhanced oxidation of SO₂ in the irradiation of NO_x-olefin mixtures in air,⁷⁸ and more recently in the presence of ozone-olefin mixture in the dark,¹⁰ may be due to the reaction of SO₂ with HO₂ produced in the ozone-olefin reaction. The rate constant for the reaction of the oxidizing species with SO₂ has been estimated to be $\sim 2 \times 10^6$ l. mol⁻¹ sec⁻¹¹⁰ while the HO₂-SO₂ rate constant has been recently determined as 5×10^5 l. mol⁻¹ sec⁻¹,⁷⁹ with an uncertainty of a factor of 3.

In addition, the unknown phytotoxicants observed in the reactions of ozone with olefins^{80,81} may be the carbonyl hydroperoxides produced by α -H abstraction.

In conclusion, it appears that the O'Neal-Blumstein treatment^{23,47} of gas-phase ozone-olefin reactions is, with some modification, in qualitative agreement with much of the experimental data presented here and in earlier papers on the chemiluminescence, intermediates, and products of these reactions. Further work on the reactions of a series of olefins at varying total pressure is in progress in order to examine this mechanism in more detail, particularly with regard to its atmospheric implications.³⁶

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