# The Mechanism of Ozone-Alkene Reactions in the Gas Phase. A Mass Spectrometric Study of the Reactions of Eight Linear and Branched-Chain Alkenes

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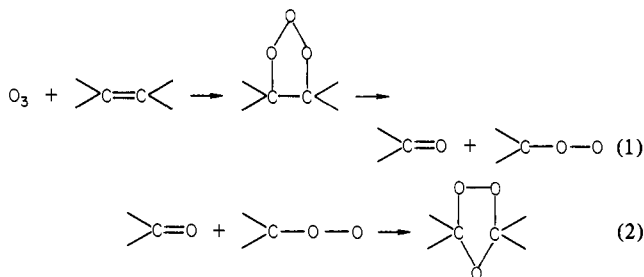
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Abstract: The stable products of the low-pressure (4–8 torr (1 torr = 133.33 Pa)) gas-phase reactions of ozone with ethene, propene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, *trans*-2-pentene, 2,3-dimethyl-2-butene, and 2-ethyl-1-butene have been identified by using a photoionization mass spectrometer coupled to a stirred-flow reactor. The products observed are characteristic of (i) a primary Criegee split to an oxoalkane (aldehyde or ketone) and a Criegee intermediate, (ii) reactions

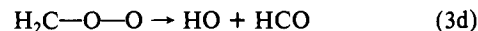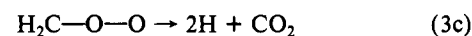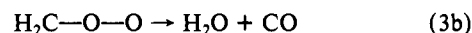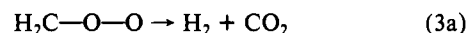$$>C=C< \; + \; O_3 \; \longrightarrow \; >C\overset{O-O}{\diagup} \; + \; >C=O$$
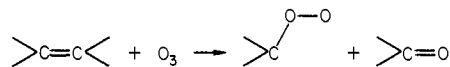
of the Criegee intermediates such as unimolecular decomposition, secondary ozonide formation, etc., and (iii) secondary alkene chemistry involving OH and other free-radical products formed by the unimolecular decomposition of the Criegee intermediates. The secondary OH–alkene–O_2 reactions account for a significant fraction of the alkene (C_nH_{2n}) consumed and lead to characteristic products such as C_n dioxoalkanes [R'C(O)C(O)R'', at m/e (C_nH_{2n} + 30)], C_n acyloins [R'C(O)CH(OH)R'', at m/e (C_nH_{2n} + 32)], and C_n alkanediols [R'CH(OH)CH(OH)R'', at m/e (C_nH_{2n} + 34)]. C_n oxoalkanes and C_n epoxyalkanes observed at m/e (C_nH_{2n} + 16) are probably formed primarily via epoxidation of the alkene by O_3. A general mechanism has been proposed to account for the observations.

There is considerable evidence[1-10] that the gas-phase reactions of ozone with alkenes can be described, at least in part, by the Criegee mechanism shown in eq 1 and 2 for solution-phase ozo-

$$O_3 \; + \; >C=C< \; \longrightarrow \; >C\overset{\displaystyle O}{\underset{\displaystyle \diagdown}{|}}\overset{\displaystyle O}{\underset{\displaystyle |}{}}C< \; \longrightarrow$$

$$>C=O \; + \; >C-O-O \quad (1)$$

$$>C=O \; + \; >C-O-O \; \longrightarrow \; >C\overset{O-O}{\underset{O}{}}C< \quad (2)$$

nolysis.[11,12] In the gas phase, however, reaction 2 is not the sole reaction of the Criegee intermediate[13] formed in reaction 1. In earlier work in our laboratory on the low-pressure (8 torr = 1.1 kPa) O_3–ethene reaction,[4] the secondary ozonide was too minor a product to be detected and the data were interpreted on the basis

of a complex sequence of free-radical reactions induced by the unimolecular decomposition of the Criegee intermediate (eq 3a–d).

$$H_2C-O-O \rightarrow H_2 + CO_2 \quad (3a)$$

$$H_2C-O-O \rightarrow H_2O + CO \quad (3b)$$

$$H_2C-O-O \rightarrow 2H + CO_2 \quad (3c)$$

$$H_2C-O-O \rightarrow HO + HCO \quad (3d)$$

Subsequent work on the O_3–propene and O_3–2-methylpropene reactions confirmed this general low-pressure mechanism.[5] In these studies it was apparent that some fraction of the alkene was being consumed in secondary hydroxyl radical reactions. Furthermore, many products have been identified in these reactions which cannot be accounted for by reactions 1 and 2 alone.[14,15] Detailed studies of the O_3–*trans*-2-butene reaction indicated that these anomalous products accounted for a significant fraction ($\sim$20–30%) of the alkene consumed.[16]

In this paper we report the mass spectra of low-pressure reacting mixtures of ozone with eight linear and branched-chain alkenes and propose a general mechanism for the O_3–alkene reaction systems to account for the major products formed in reaction 1 and in subsequent free-radical reactions.

(1) W. E. Scott, E. R. Stephens, P. L. Hanst, and R. C. Doerr, *Proc., Am. Pet. Inst., Sect. 3*, **37**, 171 (1957). The results of this and related work are discussed in ref 2, pp 159–179.

(2) P. A. Leighton, "Photochemistry of Air Pollution"; Academic Press: New York, 1961.

(3) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).

(4) J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.*, **99**, 5430 (1977).

(5) J. T. Herron and R. E. Huie, *Int. J. Chem. Kinet.*, **10**, 1019 (1978).

(6) L. B. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, **100**, 7180 (1978).

(7) H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Chem. Phys. Lett.*, **46**, 327 (1977).

(8) J. T. Herron, R. E. Huie, and J. A. Hodgeson, Eds., *NBS Spec. Publ. (U.S.)*, No. **557** (1979).

(9) M. C. Dodge and R. R. Arnts, *Int. J. Chem. Kinet.*, **11**, 399 (1979).

(10) R. I. Martinez, R. E. Huie, and J. T. Herron, *Chem. Phys. Lett.*, **72**, 443 (1980).

(11) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **49**, 13 (1977).

(12) P. S. Bailey, "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.

(13) The question as to whether the Criegee intermediate is a diradical or Zwitterion is discussed in ref 6. For the purposes of this discussion the question is unimportant, and we shall use the term "Criegee intermediate" when referring to the dioxy form >C—O—O of the intermediate.

(14) Nor could such products be explained by the O'Neal–Blumstein mechanism for O_3–alkene reactions.[15] There is now considerable evidence[1-10] against the general validity of the O'Neal–Blumstein mechanism, and, based on new kinetics information, there is general agreement {in reference 8, page 22} that the Criegee reaction pathway will be dominant under many reaction conditions.

(15) H. E. O'Neal and C. Blumstein, *Int. J. Chem. Kinet.*, **5**, 397 (1973).

(16) R. I. Martinez, R. E. Huie, and J. T. Herron, unpublished data, measured with the same instrument as was used in this work. This instrument was a modified version of one described earlier.[4,17] The vacuum envelope, constructed from stainless-steel tubing, consisted of a 6-in. o.d. front section and a 10-in. o.d. rear section. The front section, which contained the reactor and was pumped by a 6-in. oil diffusion pump, was separated from the rear section by a plate which contained a skimmer with a 2-mm diameter hole to provide collimation of the molecular beam entering the rear section. The rear section contained the ionization region and mass filter and was pumped by a 6-in. mercury diffusion lamp. Both pumps used liquid-nitrogen-cooled traps. Sealed and gettered argon and krypton resonance lamps[18] were attached via flanges. Each lamp was fitted with a light shield which had in its base a copper ring which served both as a collimator and as a photon detector to monitor lamp intensity.

Table I. Mass Spectrum of Ozone Plus Ethene Using Krypton and Argon Resonance Lamps[a]

m/e	rel intensity		probable stable products	comments
	Kr	Ar		
28 (R)	-1000	-2160		reactant ethene
29	-10	-38		
30		940	H_2CO	
31		390		fragment ion; probably H_2COH^+ from m/e 48, 60, 62, and 64
32		160	CH_3OH	possible contribution from O_2 $(a^1\Delta_g)$
33	7	39		$IP(HO_2)$ = 11.5 eV (>Kr line); assignment is therefore uncertain
34		13	H_2O_2	
42 (R + 14)	54		$H_2C{=}C{=}O$	
43	11	14		fragment ion; probably H_2CCOH^+
44 (R + 16)	21	28	CH_3CHO, $H_2C\overset{O}{\diagup\!\diagdown}CH_2$	
46		165	$HC(O)OH$	
47		57		fragment ion; probably CH_2OOH^+ from m/e 64
48	15	$(8)^b$	CH_3OOH, $CH_2(OH)_2$	
58 (R + 30)	16	17	$\overset{O}{\underset{}{HC}}{-}\overset{O}{\underset{}{CH}}$	
59	$(2)^b$			
60 (R + 32)	15	20	$\overset{O}{\underset{}{HC}}{-}\overset{OH}{\underset{}{CH_2}}$	
62 (R + 34)	8		$\overset{OH}{\underset{}{H_2C}}{-}\overset{OH}{\underset{}{CH_2}}$	
64	12	49	$(HO)CH_2(OOH)$	
67	14			

[a] $[O_3]_0$ = 1.2 × 10⁻⁸ mol cm⁻³, $[C_2H_4]_0$ = 4.2 × 10⁻⁹ mol cm⁻³, $\Delta[C_2H_4]$ = 1.8 × 10⁻⁹ mol cm⁻³, reaction time = 53 s, and total pressure = 8.4 torr. [b] Values in parentheses may be in error by as much as a factor of 4 in some cases because of background problems at that m/e with lamp indicated and, therefore, are only qualitative.

Experimental Section

The reactions were studied by using a spherical, thermostatically controlled glass reactor which was coupled to a photoionization mass spectrometer through a 200-μm sampling orifice. The instrument was a modified version[16] of one described earlier.[4,17] Ions from the mass analyzer were detected by using a Daly detector[19] and standard pulse-counting techniques, as described earlier.[4,17] Thus signals from the Daly detector were accumulated (multichannel scaling mode) under software control in a Tracor-Northern TN-11 system[20] which consists of a PDP-11/05 mini-computer, a CRT display, dual cassette tape decks, and a four-input scaler, all on the PDP-11 bus. The data, which were stored on the magnetic tape cassettes, were subsequently analyzed on the TN-11 system.

In a typical experiment, reactant flows were adjusted as desired in conjunction with the concomitant throttling of the gas flow to the pump in order to achieve the reaction time which would result in the consumption of ~40–95% of an alkene in the presence of excess ozone. [The reaction time was then estimated (by using known rate constants[21]) from the amount of alkene consumed in the presence of the excess ozone.] Mass spectra were then taken by repeatedly sweeping the mass filter and accumulating the resulting spectrum in the computer. The location of mass peaks was determined by using several known calibrants, and, on the basis of a least-squares regression analysis of mass as a function of channel number, a binomial interpolation routine was used to locate intervening mass peaks. Typically, 1–3 h of accumulation time were needed in order to completely separate minor peaks from the background [accumulation of a mass spectrum was terminated either when the most minor peak exceeded the background count rate n by more than $3n^{1/2}$ (i.e., S/N > 3) or at the end of 3 h of accumulation (a limitation imposed by the limited long-term stability of the instrumental components and the reactant flows)]. A typical difference mass spectrum, obtained by subtracting the mass spectrum of an unreacted mixture (with the ozonizer off) from the reaction mass spectrum (with the ozonizer on), is shown

(17) R. I. Martinez and J. T. Herron, *Int. J. Chem. Kinet.*, **10**, 433 (1978).
(18) R. Gordon, Jr., R. E. Rebbert, and P. Ausloos, *NBS Tech. Note* (*U.S.*), No. 496 (1969).
(19) N. R. Daly, *Rev. Sci. Instrum.*, **31**, 264 (1960).
(20) Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such an identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.
(21) R. F. Hampson and D. Garvin, Eds., *NBS Spec. Publ.* (*U.S.*), No. 513 (1978).
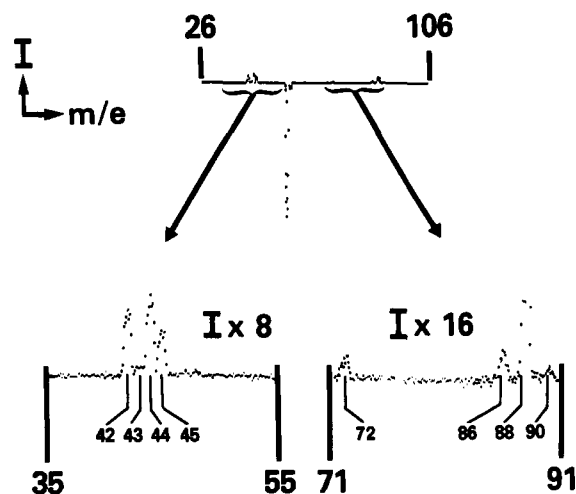

Figure 1. Difference mass spectrum (see text) for the reaction of ozone with *trans*-2-butene. Lower part of figure shows two horizontally expanded regions of interest for which the vertical display scale (ion intensity I) has also been expanded by factors of 8 and 16, respectively.

in Figure 1 for the O_3–*trans*-2-butene reaction. This shows products as positive peaks and reactants as negative peaks. Background peaks cancel.

Difference mass spectra, obtained by subtracting the mass spectrum with the ozonizer off from the mass spectrum with the ozonizer on, are given in Tables I–VIII for the reactions of ozone with ethene, propene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, *trans*-2-pentene, 2,3-dimethyl-2-butene, and 2-ethyl-1-butene. Reaction conditions are specified in each table. All experiments were done at 294 K. For the reaction with 2-ethyl-1-butene, measurements were made with an argon lamp[18] only. For the other alkenes, measurements were made with a krypton lamp (10.0- and 10.6-eV photons) and with an argon lamp (11.6- and 11.8-eV photons), neither of which is sufficiently energetic to ionize molecules such as H_2, CO, CO_2, and H_2O, which are known products of these reactions. The spectra were normalized by setting Δ(alkene) (i.e., alkene consumed), as measured with the Kr lamp, equal to -1000.

For the reaction of ozone with *trans*-2-butene, under the conditions given in Table V, final products were analyzed by gas chromatography using a Porapak PS column at 100, 130, and 150 °C. The final products were drawn from the low-pressure *stopped-flow*[4,5,17] reactor into an

Table II. Mass Spectrum of Ozone Plus Propene Using Krypton and Argon Resonance Lamps[a]

m/e	rel intensity		probable stable products	comments
	Kr	Ar		
30		154	H_2CO	
31		23		fragment ion; probably H_2COH^+ from m/e 48 and 74
32		16	CH_3OH	possible contribution from O_2 ($a^1\Delta_g$)
42 (R)	–1000	–510	$H_2C=C=O$	reactant propene and product ketene
43	–17	37		fragment ion; probably CH_3CO^+ from m/e 72 and 74, plus isotopic variant of m/e 42
44	70	79	CH_3CHO	
45	28	47		fragment ion; probably CH_3CHOH^+ from m/e 62 and 74
46		11	$HC(O)OH, CH_3CH_2OH$	
48	(4)[b]	7	$CH_3OOH, CH_2(OH)_2$	
58 (R + 16)	7	6	CH_3CH_2CHO, $(CH_3)_2CO$, $HC(O)-CH(O)$, $CH_3CH(-O-)CH_2$	
61		(4)[b]		fragment ion
62	(2)[b]		$CH_3CH(OH)_2, C_2H_5OOH$	
72 (R + 30)	5		$CH_3C(O)-CH(O)$	
74 (R + 32)	31	16	$CH_3C(O)-CH_2(OH)$, $CH_3CH(OH)-CH(O)$	the different isomers give rise to different major fragments at m/e 31 and 45
76 (R + 34)	7		$CH_3CH(OH)-CH_2(OH)$, $H_2C(O-O)CH_2 (O)$	
90 (R + 48)	(2)[b]		$CH_3CH(O-O)CH_2 (O)$	

[a] $[O_3]_0 = 6.3 \times 10^{-9}$ mol cm^{-3}, $[C_3H_6]_0 = 2.8 \times 10^{-9}$ mol cm^{-3}, $\Delta[C_3H_6] = 1.2 \times 10^{-9}$ mol cm^{-3}, reaction time = 15 s, and total pressure = 4.0 torr. [b] Values in parentheses may be in error by as much as a factor of 4 in some cases because of background problems at that m/e with lamp indicated and, therefore, are only qualitative.

evacuated sampling coil of ~5-mm i.d. The sampling coil was then pressurized to 1 atm in order to gas dynamically compress, and thus concentrate the gas sample into the end of the sampling coil containing a rubber septum. The gas sample thus pressurized and concentrated was then sampled with a gas syringe and injected into the GC. Ethanal (acetaldehyde), oxirane (ethylene oxide), *cis*- and *trans*-2,3-epoxybutane (with a *trans/cis* ratio of about 6.7), and 3-hydroxy-2-butanone (acetoin) were identified. A broad peak centered about the retention times for 2-butanone and 2,3-butanedione (diacetyl) could not be separated, but, on the basis of the different "tailing" behavior of each compound and the occurrence of corresponding mass peaks at m/e 72 and 86, it was inferred that both were present and there was more 2-butanone than 2,3-butanedione.
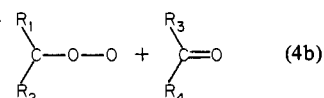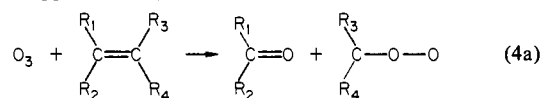
Results and Discussion

In Tables I–VIII we attempt to assign each observed peak in the mass spectra to a stable reaction product or to a fragment ion arising from a product. The number of possible isomeric species or species of the same nominal mass corresponding to any given mass spectral peak makes identification on the basis of mass spectra alone very uncertain. The identification of products here is supported in part by GC analysis of the products of the O_3–*trans*-2-butene reaction, microwave and infrared identification of products of the O_3–ethene reaction,[22,23] studies of the effects of added ethanal and nitrogen dioxide on the products of the O_3–*trans*-2-butene reaction,[10] and the existing body of data on ozone chemistry.[12] In some cases probable product identities are based solely on mechanistic considerations. In the absence of either confirmatory evidence or plausible mechanistic schemes, however, the mass spectral peaks are left unidentified. Wherever possible we have attempted to identify peaks which do not correspond to a stable product but rather are fragment ions formed by dissociative ionization of a parent product, since, even with low-energy photoionization, fragmentation is a very important process, particularly with large oxygen-containing organic molecules. For

(22) H. Kühne, S. Vaccani, A. Bauder, and Hs. H. Günthard, *Chem. Phys.*, **28**, 11 (1978).
(23) F. Su, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.*, **84**, 239 (1980).

example, in Table IX we give the mass spectra of a group of selected reaction products particularly relevant to the O_3–2-butene reaction. It can be seen that in general the krypton lamp leads to the least ambiguous mass spectra, whereas with the argon lamp fragmentation becomes much more important. For some minor products, a fragment ion but not a parent ion might be found, thus the absence of a parent ion does not rule out the presence of the corresponding product molecule. Highly speculative, but plausible, mass peak assignments have been enclosed in brackets.

A second important consideration with respect to the mass spectra is that the ion intensities do not quantitatively reflect the partial pressures of the corresponding neutral species since ion intensity is a function of both partial pressure and mass spectral sensitivity. The latter can vary widely, which explains why a very minor product such as ketene, which has a very high sensitivity, is so prominent in the spectra. This caveat is stressed in order to prevent misinterpretation of the data in Tables I–VIII.

In section A we provide a general overview of the types of reaction products that were observed and indicate their probable origins. In sections B through F we discuss in some detail the reaction mechanisms enumerated in section A. In every case, the discussion is referenced to our observations for the O_3–*trans*-2-butene reaction, since the latter has been studied over the widest range of conditions and is the one for which we have supporting GC product identification data.
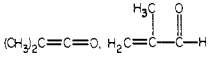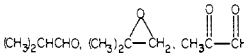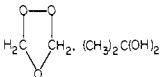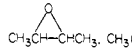
A. General Information. The most important product of the ozonation reaction is in every case the oxoalkane (aldehyde or ketone) expected on the basis of the Criegee mechanism shown in eq 4a,b. Approximately 0.9–1.0 mole of oxoalkane is produced

$$O_3 + \underset{R_2}{\overset{R_1}{>}}C=C\underset{R_4}{\overset{R_3}{<}} \longrightarrow \underset{R_2}{\overset{R_1}{>}}C=O + \underset{R_4}{\overset{R_3}{>}}C-O-O \qquad (4a)$$

$$\searrow \quad \underset{R_2}{\overset{R_1}{>}}C-O-O + \underset{R_4}{\overset{R_3}{>}}C=O \qquad (4b)$$
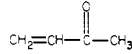
Table III. Mass Spectrum of Ozone Plus 2-Methylpropene Using Krypton and Argon Resonance Lamps[a]

m/e	rel intensity		probable stable products	comments
	Kr	Ar		
30	0.6	129	H_2CO	
31	1	8		fragment ion; probably CH_3O^+ from m/e 48 or 62 or 74
32		4	CH_3OH	possible contribution from O_2 $(a^1\Delta_g)$
34		1	H_2O_2	
40		−17		
41	−1	−94		
42	27	3	$H_2C=C=O$	probable contribution from fragment ion $(CH_3)_2C^+$ from m/e 56
43	32	83		fragment ion; probably CH_3CO^+ from m/e 58 and 74
44	16	32	CH_3CHO	
45	4	8		fragment ion; possibly CH_3CHOH^+ from m/e 60
46		10	$HC(O)OH$	
47	0.5	3		fragment ion; possibly $CH_3O_2^+$ from m/e 48 or CH_2OOH^+ from m/e 64
48	1.5	4	CH_3OOH, $CH_2(OH)_2$	
53	0.5			
54		−2		
55		−47		
56 (R)	−1000	−360		reactant 2-methylpropene
57	−40	−6		
58	262	78	$(CH_3)_2CO$	
59	51	65		fragment ion; probably $(CH_3)_2COH^+$ from m/e 76, 88, and 90
60	2.6	5	$(CH_3)_2CH(OH)$, $CH_3C(O)OH$	
61	0.7	1.7		fragment ion; probably $CH_3C(OH)_2^+$ from m/e 76
62	0.5			
64	0.5	0.7	$(HO)CH_2(OOH)$	
66	0.5			
70 (R + 14)	2.7	3.2		
71		1.3		
72 (R + 16)	31	12		
73	7	13		fragment ion; probably $CH_3C(OH)CHO^+$ from m/e 88
74	8	7		
75	10	25		fragment ion; probably $CH_3C(OH)CH_2OH^+$ from m/e 90
76	2	1.6		
81		0.6		
82	$(0.5)^b$	1.6		
84	$(0.7)^b$	1.3		
85		1		
86 (R + 30)	2			
87	0.7	1		
88 (R + 32)	4	1.4		
89	1	1.4		
90 (R + 34)	3	1		
95		1		
96	0.9	1.3		
97		0.7		
98	$(0.5)^b$	1		
101		1.3		
102		$(0.5)^b$		
103	0.7			
104 (R + 48)	1			
105	0.7	0.6		
117		0.6		
121	$(0.5)^b$			
124	$(0.5)^b$			

[a] $[O_3]_0 = 9.7 \times 10^{-9}$ mol cm^{-3}, $[C_4H_8]_0 = 1.1 \times 10^{-9}$ mol cm^{-3}, $\Delta[C_4H_8] = 7.5 \times 10^{-10}$ mol cm^{-3}, reaction time = 14 s, and total pressure = 4.1 torr. [b] Values in parentheses may be in error by as much as a factor of 4 in some cases because of background problems at that m/e with lamp indicated and, therefore, are only qualitative.

Table IV. Mass Spectrum of Ozone Plus *cis*-2-Butene Using Krypton and Argon Resonance Lamps[a]

m/e	rel intensity		probable stable products	comments
	Kr	Ar		
30		54	H_2CO	
40		-28		
41		-174		
42	69		$H_2C=C=O$	
43	12	48		fragment ion; probably CH_3CO^+ from m/e 72, 86, and 88
44	66	194	CH_3CHO, H_2C—CH_2 (O)	
45	33	89		fragment ion; probably CH_3CHOH^+ from m/e 88 and 90
46		11	$HC(O)OH$, CH_3CH_2OH	
47	[4][b]			
48	[4][b]		CH_3OOH	fragment ion; possibly $CH_3O_2{}^+$ from m/e 48
55		-85		
56 (R)	-1000	-574		reactant *cis*-2-butene
57	-43			
58	20		HC—CH (O)(O)	
70 (R + 14)	[6][b]	13	$CH_2=CH$—C—CH_3 (O)	
72 (R + 16)	12		CH_3CH—$CHCH_3$ (O), $CH_3CH_2CCH_3$ (O)	
82		17		
86 (R + 30)	[13][b]		CH_3C—CCH_3 (O)(O)	
88 (R + 32)	33	15	CH_3C—$CHCH_3$ (O)(OH)	
89	[6][b]			
90 (R + 34)	[9][b]		CH_3CH—$CHCH_3$ (OH)(OH)	
104 (R + 48)	[4][b]		CH_3CH $CHCH_3$ (O—O)(O)	
110	[2][b]			

[a] $[O_3]_0 = 3.3 \times 10^{-9}$ mol cm^{-3}, $[C_4H_8]_0 = 7.3 \times 10^{-11}$ mol cm^{-3}, $\Delta[C_4H_8] = 4.6 \times 10^{-11}$ mol cm^{-3}, reaction time = 4.1 s, and total pressure = 4.1 torr. [b] Taken under different experimental conditions: $[O_3]_0 = 3.2 \times 10^{-9}$ mol cm^{-3}, $[C_4H_8]_0 = 4.7 \times 10^{-10}$ mol cm^{-3}, $\Delta[C_4H_8] = 2.3 \times 10^{-10}$ mol cm^{-3}, reaction time = 3.1 s, and total pressure = 4.0 torr.

per mole of alkene consumed. We also find a large number of other products which, for the most part, arise from the subsequent chemistry of the Criegee intermediate.

Examination of Tables I–VIII reveals certain common features in the distribution of the products. In particular, we find products at masses corresponding to the alkene reactant (R) *plus* 16, 30, 32, 34, and in some cases 14 and 48 mass units [identified in the tables as (R + 16), (R + 30), etc.]. In the case of 2,3-dimethyl-2-butene, only the R + 16 product was observed. In only four cases do we detect the R + 48 peak of the secondary ozonide which can be formed in reaction 2. This presumably is a consequence of competing loss processes (e.g., unimolecular decomposition) for the initially formed Criegee intermediate[24] and/or low instrumental sensitivity. Titration of the Criegee intermediate by addition of aldehyde leads to enhancement of the secondary ozonide signal as a consequence of reaction 2.[10,24]

Methanal (formaldehyde) is observed at m/e 30 as a reaction product for all ozone–alkene reactions studied, even when it is not a product of the primary Criegee split (reaction 1), in which case it is probably formed by reactions of free radicals such as $CH_3\cdot$ and $CH_3O\cdot$ with O_2 and/or O_3 and probably also by reaction with O_2 of the $\cdot CH_2(OH)$ radical which for terminal alkenes may

be formed via OH–alkene reactions, as is discussed in sections B and E.

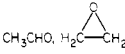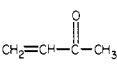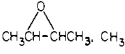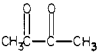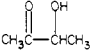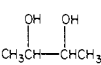An m/e 44 product peak is also observed for every O_3–alkene system studied. It is probably due mainly to ethanal, but at least in the case of O_3 + ethene and of O_3 + *trans*-2-butene, it also includes a contribution from oxirane. In the O_3–ethene reaction, m/e 44 represents an R + 16 product as is discussed in section C. In the case of the reaction of O_3 with 2-butene and with some of the other alkenes (e.g., propene, *trans*-2-pentene, etc.), m/e 44 arises from both the primary Criegee split (reaction 1) and via OH–alkene reactions, as is discussed in section B.

On the basis of its kinetic behavior,[16] the product peak at m/e 42 is almost certainly due to ketene. Although the ketene peak is a prominent feature in all the mass spectra because of the high mass spectral sensitivity of ketene, the actual amount formed is small. In the case of *trans*-2-butene, the ketene yield is only about 3% of that of ethanal. Moreover, ketene has been characterized as an R + 14 product in the case of O_3 + ethene, while, in the case of other O_3–alkene reactions, ketene could be a Criegee rearrangement product (i.e., it is formed by an intramolecular elmination which occurs subsequent to one of the possible intramolecular rearrangements of a Criegee intermediate). This is discussed in section D with reference to both C_n and C_m ketenes from C_nH_{2n} alkenes (where $m < n$). In all subsequent discussions of C_m and C_n products, we will always have $m < n$.

Secondary OH–alkene reactions, which account for a significant fraction ($\sim$13–22%) of the alkene consumed, lead to the char-

(24) J. T. Herron, R. I. Martinez, and R. E. Huie, submitted for publication.

Table V. Mass Spectrum of Ozone Plus *trans*-2-Butene Using Krypton and Argon Resonance Lamps[a]

| m/e | rel intensity | | probable stable products | comments |
	Kr	Ar		
30		167	H_2CO	
31		11		fragment ion; probably CH_3O^+ from m/e 48
32		18	CH_3OH	possible contribution from O_2 ($a^1\Delta_g$)
33		3		
34		6	H_2O_2	
40		-42		
41		-320		
42	62	14	$H_2C=C=O$	
43	7	117		fragment ion; probably CH_3CO^+ from m/e 72, 86, and 88, and $C_2H_3O^+$ from m/e 44
44	76	432	CH₃CHO, H₂C—CH₂ (epoxide)	
45	41	253		fragment ion; probably CH_3CHOH^+ from m/e 62, 88, and 90
46		19	$HC(O)OH$, CH_3CH_2OH	
47	5	19		fragment ion; probably $CH_3O_2^+$ from m/e 48 or $CH(OH)_2^+$ from m/e 62
48	4	23	CH_3OOH	
55		-129		
56 (R)	-1000	-1100		reactant *trans*-2-butene
57	-41	-38		
58	7	20	HC(O)—C(O)H	
60		12	$CH_3C(O)OH$	
61		14		
62		(3)[b]	$CH_3CH(OH)_2$	
68		(3)[b]		
70 (R + 14)		10	$CH_2=CH-C(O)-CH_3$	
72 (R + 16)	10	11	CH₃CH—CHCH₃ (epoxide), $CH_3CH_2C(O)CH_3$	
73		8		
75		(3)[b]		
82		6		
86 (R + 30)	15	6	$CH_3C(O)-C(O)-CH_3$	
88 (R + 32)	49	37	$CH_3C(O)-CH(OH)CH_3$	
89	5	6		
90 (R + 34)	8	4	$CH_3CH(OH)-CH(OH)CH_3$	

[a] $[O_3]_0 = 2.5 \times 10^{-9}$ mol cm^{-3}, $[C_4H_8]_0 = 4.4 \times 10^{-10}$ mol cm^{-3}, $\Delta[C_4H_8] = 3.1 \times 10^{-10}$ mol cm^{-3}, reaction time = 4.0 s, and total pressure = 4.1 torr. [b] Values in parentheses may be in error by as much as a factor of 4 in some cases because of background problems at that m/e with lamp indicated and, therefore, are only qualitative.

acteristic products R + 30, R + 32, and R + 34 which are discussed in section B and, with the exception of ethene, propene, and 2,3-dimethyl-2-butene, may also lead to the R + 14 products which are discussed in section D with reference to C_n conjugated oxoalkenes. While the R + 30 products derived from OH-alkene-O_2 reactions are C_n dioxoalkanes, the C_m dioxoalkanes discussed in section D are Criegee rearrangement products.

Finally, in section E we discuss the origins of both C_m and C_n acids and acid derivatives, while in section F we discuss some anomalous products.

Throughout our discussion we shall attempt to emphasize patterns among the products, whether they be characteristic or apparently anomalous for the ozone-alkene system studied.

B. Products of Secondary OH-Alkene-O_2 Reactions. In considering the mass spectrum of the ozone-*trans*-2-butene reaction in Table V and Figure 1, a particularly interesting set of peaks is the triplet at m/e 86, 88, and 90. These products together account for about 13-22% of the alkene consumed. Equivalent peaks, lying 30, 32, and 34 mass units up from the C_nH_{2n} alkene, are found in all ozone-alkene reaction mass spectra except for 2,3-dimethyl-2-butene. We believe that these are due respectively to C_n dioxoalkanes [R'C(O)C(O)R''], C_n acyloins [oxoalkanols, R'C(O)CH(OH)R''], and C_n alkanediols [R'CH(OH)CH-

(OH)R''] which are probably formed via a complex sequence of reactions initiated by reaction of hydroxyl radicals with the alkene.[10] This is discussed next with reference to 2-butene.
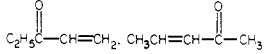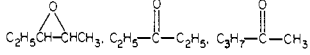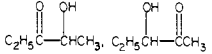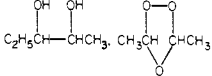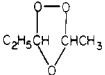
The peak at m/e 86 is probably due to 2,3-butanedione and accounts for about 2-3% of the butene consumed. As noted above, an unresolved peak from the gas chromatograph corresponded to both 2-butanone and 2,3-butanedione. From the mass spectral sensitivities of the epoxybutanes, 2-butanone, and 2,3-butanedione, the relative peak heights of m/e 72 and 86, and the relative gas-chromatographic peak areas for the epoxybutanes and the unseparated butanone and butanedione, we are able to estimate that there is about twice as much 2-butanone formed as 2,3-epoxybutane. These latter two products together account for about 2-3% of the butene consumed.

The peak at m/e 88 is due to 3-hydroxy-2-butanone (acetoin) and was confirmed by GC. It accounts for about 10-18% of the butene consumed. The corresponding product of the O_3-ethene reaction, CH(OH)CHO, has been confirmed by microwave and infrared spectroscopy.[22]

The small peak observed at m/e 90 is probably due to 2,3-butanediol.

Since with the argon lamp the magnitudes of the peaks at m/e 86, 88, and 90 decreased relative to the peak heights observed with

Table VI. Mass Spectrum of Ozone Plus *trans*-2-Pentene Using Krypton and Argon Resonance Lamps[a]

m/e	rel intensity Kr	rel intensity Ar	probable stable products	comments
28	3	1.7	C_2H_4	probably includes contribution of CH_3CH^+ fragment ion
30		12	H_2CO	
32		5	CH_3OH	possible contribution from O_2 (a$^1\Delta_g$)
34		1	H_2O_2	
42	20	-43	$H_2C=C=O$	probably includes contribution of $C_2H_5CH^+$ fragment ion from m/e 70 and 86
43	10	8		fragment ion; probably CH_3CO^+ from m/e 100 and 102
44	39	17	CH_3CHO	
45	10	6		fragment ion; probably CH_3CHOH^+ from m/e 62, 102, and 104
46	2	2	$HC(O)OH$, C_2H_5OH	
48	2	2	CH_3OOH	
55	-3	-71		
56	4		$CH_3\overset{H}{C}=C=O$	
57	9	7		fragment ion; probably $C_2H_5CO^+$ from m/e 58, 74, 86, 100 and 102
58	196	26	C_2H_5CHO, $\overset{O}{HC}-\overset{O}{CH}$	
59	20	6		fragment ion; probably $C_2H_5CHOH^+$ from m/e 102 and 104
60	1.4		$CH_3C(O)OH$, $CH_3CH_2CH_2OH$	
61	1.6	3		fragment ion
62	6	0.9	$CH_3CH(OH)_2$	
70 (R)	-1000	-54		reactant *trans*-2-pentene
71	-55	-2.4		
72	5	(0.8)[b]	$CH_3\overset{O}{C}-\overset{O}{CH}$	
74	1.6		$C_2H_5C(O)OH$, $HC(O)OC_2H_5$	
75	(1)[b]			
84 (R + 14)	(1)[b]		$C_2H_5\overset{O}{C}-CH=CH_2$, $CH_3CH=CH-\overset{O}{C}-CH_3$	
86 (R + 16)	12		$C_2H_5\overset{O}{CH}-CHCH_3$, $C_2H_5-\overset{O}{C}-C_2H_5$, $C_3H_7-\overset{O}{C}-CH_3$	
90	1.4		$CH_3CH\overset{O-O}{\underset{O}{}}CH_2$	
94	1			
100 (R + 30)	18	(0.1)[b]	$C_2H_5\overset{O}{C}-\overset{O}{C}CH_3$	
101	(2)[b]			
102 (R + 32)	11		$C_2H_5\overset{O}{C}-\overset{OH}{CH}CH_3$, $C_2H_5\overset{OH}{CH}-\overset{O}{C}CH_3$	
104 (R + 34)	2		$C_2H_5\overset{OH}{CH}-\overset{OH}{CH}CH_3$, $CH_3CH\overset{O-O}{\underset{O}{}}CHCH_3$	
118 (R + 48)	1.4		$C_2H_5CH\overset{O-O}{\underset{O}{}}CHCH_3$	

[a] $[O_3]_0 = 3.1 \times 10^{-9}$ mol cm^{-3}, $[C_5H_{10}]_0 = 6.8 \times 10^{-10}$ mol cm^{-3}, $\Delta[C_5H_{10}] = 6.1 \times 10^{-10}$ mol cm^{-3}, reaction time = 5.4 s, and total pressure = 4.0 torr. [b] Values in parentheses may be in error by as much as a factor of 4 in some cases because of background problems at that m/e with lamp indicated and, therefore, are only qualitative.

the krypton lamp, we concluded that some of the new peaks which appeared when the argon lamp was used were probably due to dissociative ionization of these larger molecules. Examination of the photoionization mass spectra of 3-hydroxy-2-butanone, 2,3-butanedione, *trans*-2,3-epoxybutane, and 2-butanone given in Table IX confirmed this hypothesis. In addition, the spectra of Table IX demonstrate that dissociative ionization can be important even when a krypton lamp is used. This may help to explain the observation by Atkinson et al.[25] of mass spectral peaks at masses corresponding to free radicals in their study of O_3–alkene
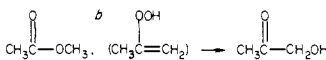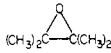
reactions. These mass peaks were probably due to ion fragments produced by dissociative ionization. Their work was possibly further complicated in the particular instrument they used (which was described in ref 26) by electron-impact ionization by photoelectrons produced by scattered photons.[26]

In a study involving the addition of radical scavengers to the ozone–*trans*-2-butene system,[10] we were able to infer that these products at m/e 86, 88, and 90 were due to secondary radical reactions (eq 6a–c and 7) arising from the reaction of the hydroxyl

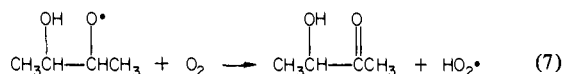(25) R. Atkinson, B. J. Finlayson, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **95**, 7592 (1973).
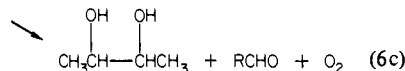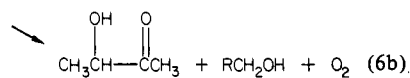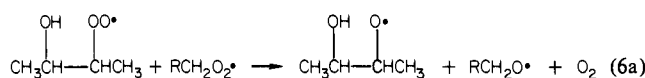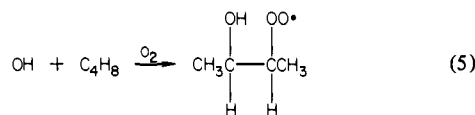
(26) R. I. Martinez, thesis, University of California, Los Angeles, 1976; *Diss. Abstr. Int. B*, **36**, 6193-B (1976).

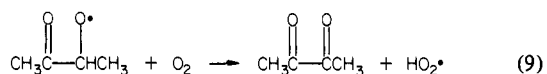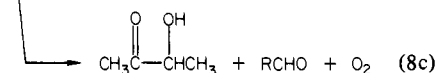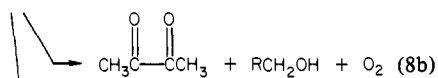**Table VII.** Mass Spectrum of Ozone Plus 2,3-Dimethyl-2-butene Using Krypton and Argon Resonance Lamps[a,b]
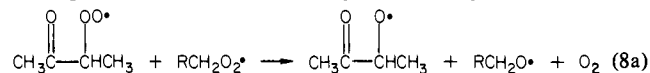
m/e	rel intensity		probable stable products	comments
	Kr	Ar		
30	−10	47	H_2CO^b	
41		3		
42	11		$H_2C=C=O$	
43	50	112		
44		7	CH_3CHO	
45		6		
48		6	CH_3OOH	
56	−2	−35		
58	731	178	$(CH_3)_2CO$	
59	91	62		fragment ion; probably $(CH_3)_2COH^+$
60		7	$CH_3C(O)OH^b$	
69	−36	−430		
70		−25		
71		−2		
72	24	10		
74	9	9		
81		6		
82		6		
84 (R)	−1000	−270		reactant 2,3-dimethyl-2-butene
85	−74	−17		
100 (R + 16)	(5)[c]			
101		6		

[a] $[O_3]_0 = 1.6 \times 10^{-9}$ mol cm^{-3}, $[C_6H_{12}]_0 = 6.2 \times 10^{-11}$ mol cm^{-3}, $\Delta[C_6H_{12}] = 5.8 \times 10^{-11}$ mol cm^{-3}, reaction time = 2.8 s, and total pressure = 4.1 torr. [b] Although not observed here, CH_3OH and $HC(O)OH$ have been reported as products by Smith and Eastman.[50] They also identified as products H_2CO, $CH_3C(O)OH$, and $CH_3C(O)OCH_3$. [c] Values in parentheses may be in error by as much as a factor of 4 in some cases because of background problems at that m/e with lamp indicated and, therefore, are only qualitative.

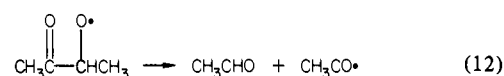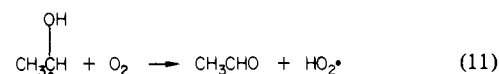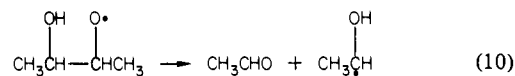radical with butene (eq 5), thus leading to 3-hydroxy-2-butanone and 2,3-butanediol.

$$OH + C_4H_8 \xrightarrow{O_2} CH_3\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OO\cdot}{C}}CH_3 \quad (5)$$

$$CH_3\overset{OH}{CH}-\overset{OO\cdot}{CH}CH_3 + RCH_2O_2\cdot \longrightarrow CH_3\overset{OH}{CH}-\overset{O\cdot}{CH}CH_3 + RCH_2O\cdot + O_2 \quad (6a)$$

$$\searrow CH_3\overset{OH}{CH}-\overset{O}{C}CH_3 + RCH_2OH + O_2 \quad (6b)$$

$$\searrow CH_3\overset{OH}{CH}-\overset{OH}{CH}CH_3 + RCHO + O_2 \quad (6c)$$

$$CH_3\overset{OH}{CH}-\overset{O\cdot}{CH}CH_3 + O_2 \longrightarrow CH_3\overset{OH}{CH}-\overset{O}{C}CH_3 + HO_2\cdot \quad (7)$$

2,3-Butanedione probably arises from similar reactions (eq 8a–c and eq 9) The source of the $CH_3C(O)C(CH_3)(H)OO\cdot$ radical

$$CH_3\overset{O}{C}-\overset{OO\cdot}{CH}CH_3 + RCH_2O_2\cdot \longrightarrow CH_3\overset{O}{C}-\overset{O\cdot}{CH}CH_3 + RCH_2O\cdot + O_2 \quad (8a)$$

$$\searrow CH_3\overset{O}{C}-\overset{O}{C}CH_3 + RCH_2OH + O_2 \quad (8b)$$

$$\searrow CH_3\overset{O}{C}-\overset{OH}{CH}CH_3 + RCHO + O_2 \quad (8c)$$

$$CH_3\overset{O}{C}-\overset{O\cdot}{CH}CH_3 + O_2 \longrightarrow CH_3\overset{O}{C}-\overset{O}{C}CH_3 + HO_2\cdot \quad (9)$$

is not known, although its presence, along with the radical products of reactions 5, 6a, and 8a, has been inferred from scavenging experiments by using NO_2.[10]

In addition to the ethanal produced via the Criegee split, significant amounts of ethanal probably also result from the OH–trans-2-butene–O_2 reaction system[27] via such reactions as eq 10–12. (See, however, comments and discussion on this type of reaction in ref 8.)

$$CH_3\overset{OH}{CH}-\overset{O\cdot}{CH}CH_3 \longrightarrow CH_3CHO + CH_3\overset{OH}{CH} \quad (10)$$

$$CH_3\overset{OH}{CH} + O_2 \longrightarrow CH_3CHO + HO_2\cdot \quad (11)$$

$$CH_3\overset{O}{C}-\overset{O\cdot}{CH}CH_3 \longrightarrow CH_3CHO + CH_3CO\cdot \quad (12)$$
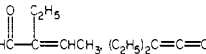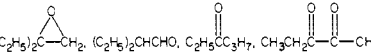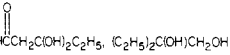
The types of reactions shown above can be written for all the alkenes considered here, except for 2,3-dimethyl-2-butene. For the linear, nonsymmetric alkenes, isomeric hydroxy-substituted oxo compounds are possible, which, although they have the same mass, will have different ion fragmentation patterns. Fragments corresponding to the different isomers can be found (see, for example, Table II).

C. Products of Alkene Epoxidation Reactions. For the O_3–trans-2-butene reaction, the peak at m/e 72 is due to 2,3-epoxybutane and 2-butanone. These two products together account for about 2–3% of the butene consumed, and as was indicated above, there is about twice as much 2-butanone as there is 2,3-epoxybutane. Both cis- and trans-epoxybutanes were found, with a trans-to-cis ratio of about 6.7. Epoxides and oxoalkanes arising from the parent alkene are known to be products of the solution phase ozonation of alkenes, but there remains some uncertainty as to the mechanism of their formation. In his recent review, Bailey[12] favored a mechanism, in eq 13a,b, in which ozone adds

(27) H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.*, **82**, 135 (1978).

Table VIII. Mass Spectrum of Ozone Plus 2-Ethyl-1-butene Using an Argon Resonance Lamp[a,b]

m/e	rel intensity Ar	probable stable products	comments
28	20	C_2H_4	probably includes contribution of CH_3CH^+ fragment ion
30	380	H_2CO	
31	23		fragment ion; probably H_2COH^+ and/or CH_3O^+ from m/e 48
34	6	H_2O_2	
41	-16		
42	-172		
44	140	CH_3CHO	
45	42		fragment ion; probably $C_2H_5O^+$ from m/e 62 and m/e 120 [$HOCH_2CH_2C(OH)_2C_2H_5$] and/or m/e 134 [$HOCH_2CH_2C(OH)(C_2H_5)CH_2OH$] and/or $COOH^+$ from m/e 46 and/or 74
46	35	$HC(O)OH, C_2H_5OH$	
47	8		fragment ion; probably $CH_3O_2{}^+$ from m/e 48
48	11	$CH_3OOH, CH_2(OH)_2$	
54	-46		
55	-262		
56	-737		
57	514		fragment ion; probably $C_2H_5CO^+$ from m/e 86 and/or 100
59	19		fragment ion; probably $C_2H_5CHOH^+$ from m/e 88 or CH_2COOH^+ from m/e 74
62	12	C_2H_5OOH	
69	-2362		
70	-112		
71	55		fragment ion; probably $(C_2H_5)_2CH^+$ from m/e 100 and/or 88
72	34	$C_2H_5\overset{O}{\overset{\|}{C}}CH_3$	
73	10		fragment ion; probably $(C_2H_5)CH(OH)CH_2{}^+$ from m/e 88
74	19	$C_2H_5C(O)OH$	
76	3	$H_2C\overset{O-O}{\overset{\diagup\diagdown}{\quad}}CH_2$	
82	14		
83	0.8		
84 (R)	-1000		reactant 2-ethyl-1-butene
85	-50		
86	390	$(C_2H_5)_2CO$	
87	189		fragment ion; probably $(C_2H_5)_2COH^+$ from m/e 118 and/or 116 [$(C_2H_5)_2C(OH)CHO$] and $C_2H_5C(OH)CHO^+$ from m/e 116
88	31	$(C_2H_5)_2CH(OH)$	
89	44		fragment ion; probably $C_2H_5C(OH)_2CH_2{}^+$ from m/e 118 and/or 120 [$C_2H_5C(OH)_2CH_2CH_2OH$] and/or $HOCH_2C(OH)(C_2H_5)^+$ from m/e 118 and 132 [$HC(O)CH_2C(OH)(C_2H_5)CH_2OH$] and/or 134 [$HOCH_2CH_2C(OH)(C_2H_5)CH_2OH$]
95	6		
96	2		
98 (R + 14)	14	$HC\overset{O}{\overset{\|}{-}}C\overset{C_2H_5}{\overset{\|}{-}}=CHCH_3,\ (C_2H_5)_2C=C=O$	
99	14		fragment ion; probably $(C_2H_5)_2C(CHO)^+$ from m/e 116 [$(C_2H_5)_2C(OH)CHO$]
100 (R + 16)	104	$(C_2H_5)_2C\overset{O}{\overset{\diagup\diagdown}{\quad}}CH_2,\ (C_2H_5)_2CHCHO,\ C_2H_5\overset{O}{\overset{\|}{C}}C_3H_7,\ CH_3CH_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$	
101	16		fragment ion; probably $(C_2H_5)_2C(CH_2OH)^+$ from m/e 118 and/or $HC(O)CH_2C(OH)(C_2H_5)^+$ from m/e 132 [$HC(O)CH_2C(OH)(C_2H_5)CH_2OH$]
103	50		fragment ion; probably $HOCH_2CH_2C(OH)C_2H_5{}^+$ from m/e 120 [$HOCH_2CH_2C(OH)_2C_2H_5$] and/or 134 [$HOCH_2CH_2C(OH)(C_2H_5)CH_2OH$]
112	3		
113	5		
114 (R + 30)	8		
115	6		fragment ion; possibly $HC(O)CH_2C(C_2H_5)CH_2OH^+$ from m/e 132 [$HC(O)CH_2C(OH)(C_2H_5)CH_2OH$]
117	7		fragment ion; possibly $HOCH_2CH_2C(C_2H_5)CH_2OH^+$ from m/e 134 [$HOCH_2CH_2C(OH)(C_2H_5)CH_2OH$]
118 (R + 34)	4	$H\overset{O}{\overset{\|}{C}}CH_2C(OH)_2C_2H_5,\ (C_2H_5)_2C(OH)CH_2OH$	
121	6		
123	4		
124	6		
125	3		

[a] $[O_3]_0 = 9.6 \times 10^{-9}$ mol cm^{-3}, $[C_6H_{12}]_0 = 6.5 \times 10^{-10}$ mol cm^{-3}, $\Delta[C_6H_{12}] = 4.9 \times 10^{-10}$ mol cm^{-3}, reaction time = 14 s, and total pressure = 4.1 torr. [b] Quantitative observations were not possible beyond m/e 130 due to background noise problems.

(13a)

(13b)
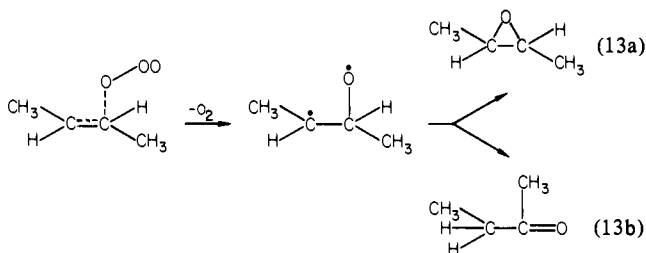
directly to the alkene. A different mechanism involving epoxidation by the Criegee intermediate has been given very strong support by Hinrichs et al.[28] in a study in which the Criegee intermediate was produced in the absence of ozone. Possibly, either mechanism could be important, depending upon the reactant and the solvent. However, the addition of a 20-fold excess of ethanal to the low-pressure ozone–*trans*-2-butene reaction system led to a doubling of the yield (per mole of butene consumed) of m/e 72.[29] This suggests that these products do not arise from reactions of a stabilized Criegee intermediate under these conditions. The *apparent* yield increase is a consequence of the fact that in the presence of added ethanal the butene is no longer being consumed by hydroxyl radicals. Thus, it rules out the involvement of hydroxyl radicals in the formation of products at m/e 72 via reactions such as those proposed by Morris et al.[30] for OH–alkene reactions in the absence of added O_2. The work of Niki et al.[27] provides additional support for this conclusion. Therefore, we conclude that under our experimental conditions, these epoxides and oxoalkanes arise from a primary ozonation reaction, as discussed by Bailey.[12,31] Oxirane and ethanal, which are known products of the O_3–C_2H_4 reaction[22] and which correspond to the observed m/e 44 peak in Table I, are probably also formed via reactions analogous to (13a) and (13b).

D. Dioxoalkanes, Ketenes, and Conjugated Oxoalkenes. (i) C_m Dioxoalkanes. For the O_3–*trans*-2-butene reaction, the peak

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(28) T. A. Hinrichs, V. Ramachandran, and R. W. Murray, *J. Am. Chem. Soc.*, **101**, 1282 (1979).

(29) R. I. Martinez, J. T. Herron, and R. E. Huie, unpublished data. Under our experimental conditions, with $[trans\text{-}2\text{-}C_4H_8]_0 \simeq (1.1 \pm 0.07) \times 10^{-9}$ mol cm^{-3}, the fractions of *trans*-2-butene (T2B) consumed in the presence and absence of added CH_3CHO {≡A} were respectively $F_{T2B}{}^A = \Delta[T2B]^A/[T2B]_0 = 0.27$ and $F_{T2B}{}^{no\,A} = \Delta[T2B]^{no\,A}/[T2B]_0 = 0.4_2$, and $\alpha_{T2B} = F_{T2B}{}^{no\,A}/F_{T2B}{}^A = 1.6$. In the presence of added CH_3CHO, with $[CH_3CHO]_0/[O_3]_0/[T2B]_0 \simeq 20\!:\!8\!:\!1$, more than 75% of any OH produced by secondary reactions should have been scavenged by the CH_3CHO instead of reacting with the T2B. Hence, for any product X, by comparing its yield per mole of T2B consumed, Y_X {≡$\Delta[X]/\Delta[T2B]$}, in the presence of added excess CH_3CHO, $Y_X{}^A$, relative to its product yield in the absence of added CH_3CHO, $Y_X{}^{no\,A}$, one can infer whether or not X is a product of secondary reactions initiated by OH–alkene reactions. Thus, by making the simplifying assumption that T2B is consumed primarily by O_3 and OH, we concluded, on the basis of the measured R_X {≡$Y_X{}^A/Y_X{}^{no\,A}$}, that while diacetyl, acetoin, and 2,3-butanediol certainly arise from OH–T2B-initiated reactions ($R_X \approx 0.3$–0.4; see also ref 10], m/e 72 (2-butanone and 2,3-epoxybutane) appears to arise from O_3–T2B-initiated reactions such as (13a) and (13b) ($R_X \approx 2$) and *not* from OH–T2B-initiated reactions ($R_X \approx 0.4$). Also, for m/e 58 [(HCO)$_2$], $R_X \approx 1$. This suggests that (HCO)$_2$ does not arise via OH–T2B chemistry but probably from O_3–T2B-initiated reactions. However, the relatively low R_X value also suggests that the (HCO)$_2$ precursor may be partially consumed by the added CH_3CHO. This is suggestive of a precursor such as the excited Criegee intermediate,[24] which is effectively titrated (i.e., quenching plus scavenging of the excited Criegee intermediate) by added CH_3CHO in competition with its rearrangement to glyoxal.
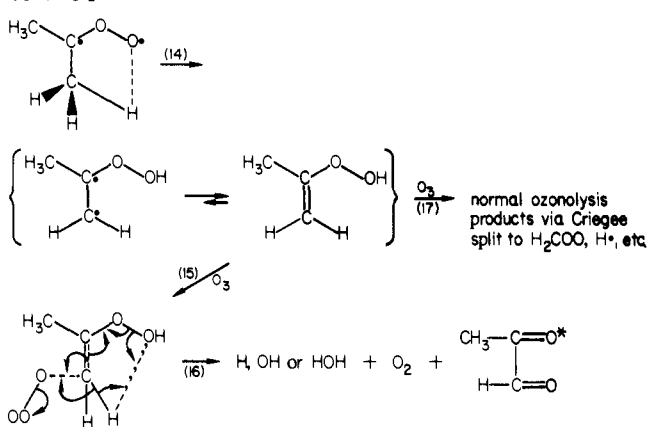
(30) E. D. Morris, Jr., D. H. Stedman, and H. Niki, *J. Am. Chem. Soc.*, **93**, 3570 (1971).

(31) An alternative path for epoxyalkane formation, suggested by Harding and Goddard[6] with reference to oxirane formation in the gas-phase O_3–C_2H_4 reaction, is the intramolecular elimination of O_2, ($a^1 \Delta g$) from the primary
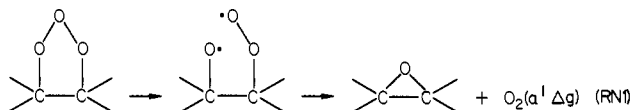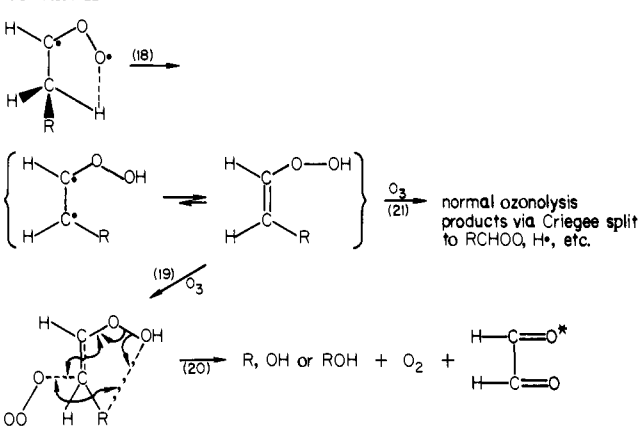
ozonide. Under our experimental conditions we cannot distinguish between reactions (13a) and (RN1) as the source of epoxyalkane.


Scheme I

normal ozonolysis products via Criegee split to H_2COO, H•, etc.

H, OH or HOH + O_2 +

Scheme II

normal ozonolysis products via Criegee split to RCHOO, H•, etc.
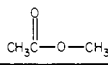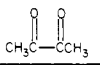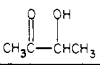
R, OH or ROH + O_2 +

at m/e 58 is probably due to dioxoethane (ethanedial, glyoxal) since its phosphorescence has been identified in the O_3–2-butene systems.[32,33] (For the other alkenes studied, the m/e 58 peak may also correspond to other products, as indicated in Tables I–VIII.) The source of the glyoxal is not known. We have observed, however, that the addition of a 20-fold excess of ethanal to the reacting system resulted in no change in the yield of dioxoethane per mole of butene consumed.[29] If dioxoethane was to arise from hydroxyl radical initiated reactions or from the stabilized Criegee intermediate, the yield would have been expected to decrease by a factor of about 2. Further, in their studies of the chemiluminescence from ozone–alkene systems, Schurath et al.[33] reported that dioxoethane phosphorescence is observed only for alkenes such as $R'CH_2C(H)$=$CR''R'''$ and $R'CH_2C(H)$=$C(H)CH_2R''$, while 1,2-dioxopropane (methylglyoxal) phosphorescence is observed only for alkenes such as $(CH_3)_2C$=$CR'R''$ and $(CH_3)_2C$=$C(CH_3)_2$ (where R', R'', $R''' = H$ or alkyl). Also, this phosphorescence was independent of added O_2.

These observations can be rationalized by assuming that the dioxoalkane phosphorescence is a consequence of a rearrangement of the excited Criegee intermediate,[24] a primary product of the ozone–alkene reaction. If the phosphorescent dioxoalkane was to arise from a direct ozone–alkene interaction, as do the epoxyalkanes, then its yield would be expected to increase upon addition of ethanal. Hence, the constant dioxoalkane yield probably reflects a competition between the rearrangement process, and quenching and scavenging of the excited Criegee intermediate by the ethanal.[24] Thus, consistent with the above observations, we propose the chemiexcitation mechanism of Scheme I for methylglyoxal from 2-methylpropene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene [all of which produce methylglyoxal

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(32) B. J. Finlayson, J. N. Pitts, Jr., and R. Atkinson, *J. Am. Chem. Soc.*, **96**, 5356 (1974).

(33) U. Schurath, H. Güsten, and R. D. Penzhorn, *J. Photochem.*, **5**, 33 (1976).

Table IX. Mass Spectra of Selected Reaction Products of Ozone–Alkene Reactions Using Krypton and Argon Resonance Lamps[a]

m/e	CH₃CH=O Kr	Ar	CH₃CCH₃ Kr	Ar	C₂H₅CCH₃ Kr	Ar	CH₃CH–CHCH₃ Kr	Ar	CH₃C–O–CH₃ Kr	Ar	CH₃C–CCH₃ Kr	Ar	CH₃C–CHCH₃(OH) Kr	Ar
28							0.9	5						
29		3						7						
31										9				
32										8				
39														0.8
41														1
42			1	1		0.4	4	5						
43		306	10	68	4	44	867	685	3	1400	132	156	6	23
44	1000	1890	0.4	2		2	471	1470		38	5	7		3
45	23	45				0.3	13	52		15		0.8	410	388
46	2	4					2	4						10
57					10	23	39	40						
58			1000	190	2	0.9	8	3			5			
59			38	6		0.1								2
60			3	0.7										2
71								8						
72					1000	148	1000	137			3	0.8	23	33
73					49	7	46	6						
74					3	0.6	3		1000	1560				
75									32	55				
76									6	7				
86											1000	133	32	5
87											51	7	11	
88											6	0.9	1000	100
89													45	6
100											2[b]	0.3[b]		
114													100[b]	13[b]

[a] Normalized to parent peak = 1000 using the krypton lamp.   [b] Impurity peaks.

phosphorescence[33] and yield the (CH₃)₂COO Criegee intermediate], while we propose Scheme II for glyoxal from alkenes which yield RCH₂CHOO Criegee intermediates,[33] where R = H· for propene and *cis*- and *trans*-2-butene, CH₃· for 1-butene, and HC(O)CH₂CH₂CH₂· for cyclohexene.[33] These reactions are discussed next.

Reaction 14 is important in the solution-phase chemistry of O₃ + 2,3-dimethyl-2-butene,[12] and reaction 18 is its analogue. Reaction 17 was proposed by Wadt and Goddard[3] as a source of hydrogen atoms and H₂ĊOO· in the gas-phase reaction of O₃ with 2,3-dimethyl-2-butene. [These products will be discussed in section F with reference to OH Meinel band chemiluminescence and H₂CO (¹A″) production in ozone–alkene systems.] By analogy with reaction 13b, we propose reactions 15 and 19 as the sources of excited glyoxal and methylglyoxal. In the case of O₃ + *cis*-2-butene, the measured specific rate of phosphorescent emission from glyoxal[32] suggests that reaction 20 accounts for less than 10⁻³% of the butene consumed, while the measured specific rates of emission from OH and H₂CO[32] suggest that (21) accounts for less than 10⁻⁵% of the butene consumed. Clearly, reactions such as (19)–(21), and by analogy probably also (15)–(17), are very minor processes in O₃–alkene systems.

The chemiexcitation mechanism proposed above would explain why glyoxal phosphorescence is not observed in the O₃–ethene system, even though glyoxal is a known product of the reaction (see Table I and section B with reference to OH–alkene reactions as sources of Cₙ dioxoalkanes). Clearly, reactions 14 and 18 are not possible for H₂COO (e.g., from O₃ + C₂H₄). Furthermore, according to the proposed mechanism, the formation of excited 2,3-butanedione would not be expected for any of the alkenes discussed, and therefore in the absence of other excitation mechanisms, diacetyl phosphorescence should not be observed in any of the O₃–alkene systems discussed. Such was found to be the case.[32,33] Diacetyl chemiexcitation by the proposed mechanism might occur for an alkene such as
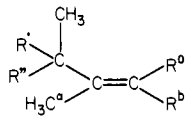

where various R′ and R″ substituents would have to be tested, including H and CH₃. However, this too would not necessarily provide positive evidence for the proposed mechanism because the dynamics of the intramolecular rearrangement reactions (14) and (18) may preferentially involve intramigration of the H atoms of the Cᵅ, resulting in formation of (CH₃)(R′)(R″)C–C(O)–C-(O)H instead of diacetyl.

It is interesting to note that glyoxal (m/e 58) is produced in both the O₃–*cis*-2-butene and O₃–*trans*-2-butene systems (see Tables IV and V). This suggests that the syn–anti isomers of the Criegee intermediate which is involved in reaction 18 do readily interconvert in the gas phase, as has been proposed by Harding and Goddard.[6] The calculated barrier to syn–anti interconversion is sufficiently high so that in solution the isomers will not interconvert, and, on the basis of conformational analysis of primary ozonides, *trans*-alkenes produce only syn isomers while *cis*-alkenes produce only anti isomers.[6,12] Hence, if the syn–anti isomers did not interconvert in the gas phase, glyoxal would be produced only by the syn isomer and thus only in the O₃–*trans*-2-butene reaction and not in the O₃–*cis*-2-butene reaction.

Examination of Tables I–VIII shows that the presence or absence of product peaks at m/e 58 (glyoxal) and m/e 72 (methylglyoxal) is in general agreement with the proposed chemiexcitation mechanism, reactions 15 and 19. However, for several of the alkenes, these peaks also correspond to other products or to these same products but from other sources such as the OH–alkene reactions discussed in section B. For example, it is especially noteworthy that the same dioxoalkane, glyoxal, can be either a Cₘ or Cₙ product, depending on its origin. Thus, while glyoxal is a Cₙ product of the OH–ethene reaction, it is a Cₘ product of the O₃–2-butene reaction, produced by the proposed chemiexcitation mechanism. Similarly, while methylglyoxal is a Cₙ product of the OH–propene reaction, it is a Cₘ product of the O₃–2,3-dimethyl-2-butene reaction, produced by the proposed chemiexcitation mechanism. This was not immediately obvious and probably delayed the characterization of the various mechanisms responsible for the same functional-class compounds.

An alternate route to Cₘ dioxoalkanes is suggested as a possibility by the proposal of Wadt and Goddard[3] that, in addition to undergoing reaction 17 [and by analogy (21)], the hydroper-

oxide formed in reaction 14 [and by analogy in (18)] might also decompose by losing an OH group. Then, in the presence of O_2


$$R'—C=O$$
$$R''—C=O \quad (22)$$
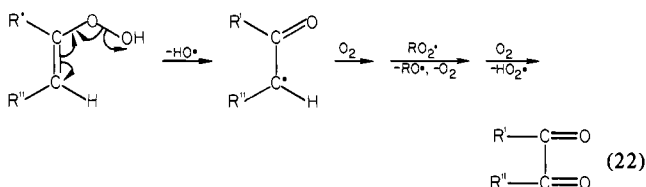
where the hydroperoxide $R'C(OOH)CHR''$ is formed by rearrangement of an initially formed Criegee intermediate in a reaction analogous to (14) and (18). The O_3–1-butene and/or O_3–*trans*-2-pentene reactions in the presence and absence of O_2 would provide a unique test of the possible validity of reaction 22. The observation of m/e 72 from O_3–*trans*-2-pentene (see Table VI; presumed to be methylglyoxal based on reaction 22, with R' = H, R'' = CH_3) provides some support for this hypothesis, although GC identification is still necessary.

(ii) **C_m Ketenes.** For the C_nH_{2n} alkenes studied, examination of Tables I–VIII also reveals product peaks which correspond to C_m ketenes ($m < n$); e.g., ketene from O_3 + 2-butene in Tables IV and V, and both ketene (m/e 42) and methylketene (m/e 56) from O_3 + *trans*-2-pentene in Table VI. In the case of O_3 + *trans*-2-butene, the yield of ketene was about 0.03–0.04 mol/mole of butene consumed. One can readily account for all the observed C_m ketenes if the hydroperoxide $R'C(OOH)CHR''$, which is formed by rearrangement of an initially formed Criegee intermediate in a reaction analogous to (14) and (18), undergoes the intramolecular elimination processes indicated in Scheme III. Reaction 27 is the well-known Wolff rearrangement.[34]

(iii) **C_n Ketenes and Conjugated C_n Oxoalkenes.** Examination of Tables I–VIII indicates that for most C_nH_{2n} alkenes there are product peaks designated in the tables as R + 14 which correspond to C_n-substituted ketenes (e.g., in Table I, O_3 + C_2H_4 → ketene[22]) and/or C_n conjugated oxoalkenes (e.g., in Tables IV and V, O_3 + 2-C_4H_8 → 3-buten-2-one[32]). Ketene has been confirmed as a product of the O_3–C_2H_4 reaction by microwave spectroscopy.[22] Its production in the O_3–C_2H_4 reaction obviously cannot be explained on the basis of an isomerized Criegee intermediate.[35] 3-Buten-2-one has been confirmed as a product of the O_3–2-butene reaction by gas chromatography;[32] it was observed only in the presence of added O_2. This suggests that the 3-buten-2-one is a product of secondary radical reactions, probably initiated by OH addition to the butene.

Scheme III
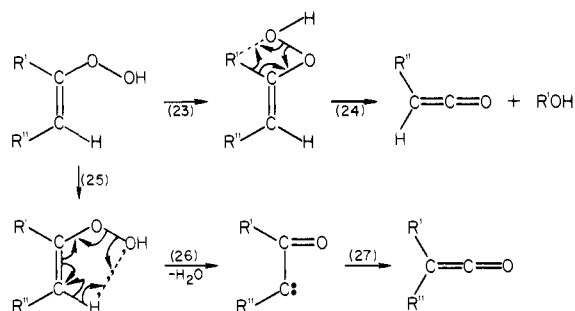
(34) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw-Hill: New York, 1968.

(35) Ketene was observed as a product of the O_3–ethanal reaction (unpublished data). Ethanal is a known product of the O_3–ethene reaction.[22] Hence the ketene observed in the O_3–ethene reaction may have been produced by addition of O_3 to the product ethanal. However, because of their relative specific rates,[2] the secondary O_3–CH_3CHO reaction would become important relative to an O_3–alkene reaction only under conditions of excess O_3 after most of the alkene would have been consumed. The observation of ketene from O_3 + CH_3CHO led to an examination of the recent work of several investigators. This indicated that the currently accepted O_3–aldehyde reaction mechanism was incomplete. An alternative mechanism has been proposed[36] to explain the observations.
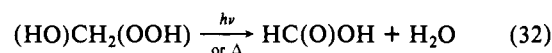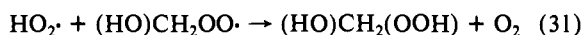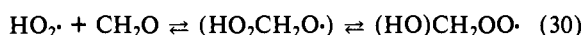
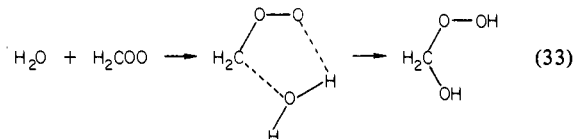(36) R. I. Martinez, *Int. J. Chem. Kinet.*, in press.

Scheme IV
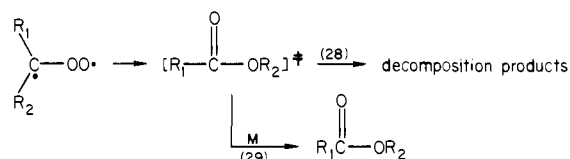
E. C_m and C_n Alkanoic Acids and Acid Derivatives. A puzzling feature of the low-pressure stopped-flow studies of the O_3–ethene[4] and O_3–propene[5] reactions was the induction times found for methanoic (formic) and ethanoic (acetic) acid formation. In addition, alkanoic acid yields from ozone–alkene reactions ($\sim$ 0.05–0.08 mol acid/mol of alkene consumed) appear to be substantially independent of the total pressure.[4,7,23] These observations seem to rule out simple quenching of an isomerized Criegee intermediate as a significant source of alkanoic acids and acid derivatives (Scheme IV).[24] Also, the induction times would rule out the *direct* production of the acids from the reactions of OH or HO_2 radicals with oxo compounds (aldehydes and ketones).

A possible explanation for the observed induction times is that the alkanoic acids arise from the thermal decomposition of compounds such as $(HOO)CR'R''(OH)$, possibly produced by secondary reactions involving HO_2 addition to oxo compounds. For example, the thermal and photochemical decomposition of $(HOO)CH_2(OH)$ has been implicated as one source of methanoic acid in the photooxidation of methanal.[37,38] Their suggested mechanism is shown in eq 30–32. The possibility that reaction 32 is

$$HO_2\cdot + CH_2O \rightleftarrows (HO_2CH_2O\cdot) \rightleftarrows (HO)CH_2OO\cdot \quad (30)$$

$$HO_2\cdot + (HO)CH_2OO\cdot \rightarrow (HO)CH_2(OOH) + O_2 \quad (31)$$

$$(HO)CH_2(OOH) \xrightarrow[\text{or } \Delta]{h\nu} HC(O)OH + H_2O \quad (32)$$

the source of methanoic acid in the O_3–ethene reaction is supported by the observation of a product peak at m/e 64 (see Table I), a fairly unique mass, corresponding to $(HOO)CH_2(OH)$. However, it seems unlikely that the rate of reaction 30 is fast enough to produce $(HOO)CH_2(OH)$ in our system.[39] An alternate path (eq 33) involves addition of H_2O to the stabilized Criegee intermediate.[12,24] This would provide an atmospherically important loss process for the Criegee intermediate[24] but cannot explain $(HOO)CH_2(OH)$ formation under our low-pressure conditions. The reaction sequence (33) + (32) is discussed in detail elsewhere[24] with reference to its postulated role in O_3–alkene–SO_2 systems.

Scheme V
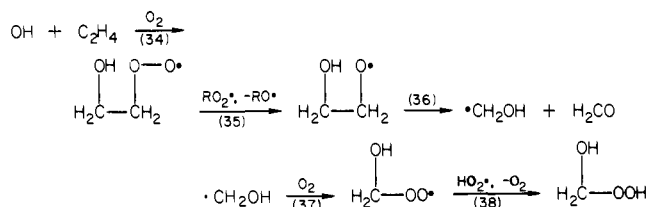
(37) F. Su, J. G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage, and L. D. Breitenbach, *Chem. Phys. Lett.*, **65**, 221 (1979).

(38) F. Su, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.*, **83**, 3185 (1979).

(39) Parent product peaks corresponding to the homologous (HOO)-$CR'R''(OH)$, where $R'R''C=O$ are the oxo compounds produced via reactions 4, were not observed for any oxo compound other than $H_2CO[(HOO)$-$CR'R''(OH)$ product peak at m/e 64] and then only in the O_3–ethene and O_3-2-methylpropene reactions, even though H_2CO is a significant product of every O_3–alkene reaction studied.

An alternate path for $(HOO)CH_2(OH)$ formation specific to ethene is shown in Scheme V, where reaction 38 is from Su et al.[37,38] However, Niki et al.[27] deduced that (37) constitutes a minor path, with >97% of the $\cdot CH_2OH$ reacting via (39) instead of (37),

$$\cdot CH_2OH + O_2 \rightarrow H_2CO + HO_2 \cdot \qquad (39)$$

as has been confirmed recently by Radford.[40] Moreover, the homologous $(HOO)CR'R''(OH)$, which would have been expected from analogous OH–alkene–O_2 reactions, were not observed.[39]

An additional source of alkanoic acids was suggested by the study of Horowitz et al.[41] and by our observation that when a large excess of ethanal is added to the O_3–*trans*-2-butene system, the yield of methanoic acid drops, while that of ethanoic acid increases. This suggested suppression of reaction 40c ($k_{40a} \gg k_{40b}$ and $k_{40c} \simeq 2k_{40b}$) due to scavenging of HO radicals by ethanal with the
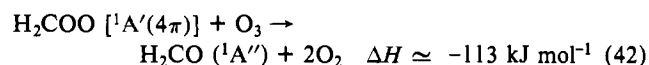
$$HO + H_2CO \rightarrow H_2O + HCO \qquad (40a)$$

$$\rightarrow H_2O + HCO^* \qquad (40b)$$

$$\rightarrow HC(O)OH + H \qquad (40c)$$
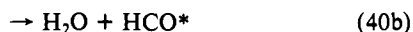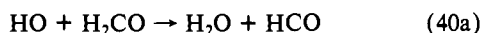
consequent generation of ethanoic acid via (41b). However (41a)

$$HO + CH_3CHO \rightarrow HC(O)OH + CH_3 \qquad (41a)$$

$$\rightarrow CH_3C(O)OH + H \qquad (41b)$$
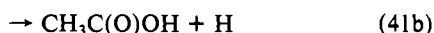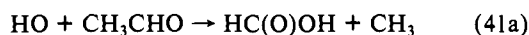
probably predominates over (41b), because of the relative bond strengths of the C–C and C–H bonds involved in reaction 41. Hence, (41) probably cannot explain our observation.

Finally, we found no evidence for the formation of methanoic acid anhydride in the O_3–ethene reaction, as has been reported.[22,23] However, examination of reaction conditions suggests that the anhydride is a product of a pressure-dependent process whose rate is probably dependent on $[O_3]^p[C_2H_4]^q[M]^r$. Thus, Kühne et al.[22] found the anhydride for $[O_3] = [C_2H_4] = 1-2$ torr (total pressure $P_t = 2-4$ torr, $T = 240-300$ K, reaction time $\tau \simeq 20-40$ s) but *not* for $[O_3] = [C_2H_4] = 10-50$ mtorr ($P_t = 20-100$ mtorr, $T = 220-300$ K, $\tau \simeq 2-100$ s). On the other hand, Su et al.[23] observed the anhydride with $[O_3] \simeq [C_2H_4] \simeq 7$ mtorr ($P_t = 700$ torr, $T = 291-299$ K, $\tau = 0-65$ min), while we observed no anhydride for $[O_3] \simeq 200$ mtorr, $[C_2H_4] \simeq 80$ mtorr ($P_t \approx 8$ torr, $T \approx 300$ K, $\tau \approx 50$ s). Furthermore, when observed, Kühne et al.[22] found an anhydride yield of only $\sim 0.8\%$ on the basis of $\Delta[C_2H_4]$, while Su et al.[23] found $\sim 18-29\%$ yield on the basis of $\Delta[C_2H_4]$ (when CO, H_2CO, and SO_2 were not included as additives).

F. "Anomalous" Products. (i) Chemiluminescent Species. The discussion of section D on C_m dioxoalkanes in terms of the reactions of the primary Criegee intermediates provides a basis for discussion of the observations by Finlayson et al.[32] of OH and H_2CO chemiluminescence from O_3–alkene reactions in the presence and absence of O_2. Thus reaction 14 followed by reaction 17 was proposed by Wadt and Goddard[3] as a source of H atoms in order to rationalize the OH ($X^2\Pi_i)_{v' \leq 9}$ Meinel bands (generated by $H + O_3 \rightarrow OH^\dagger + O_2$) observed in the O_3–2,3-dimethyl-2-butene reaction.[32] The intent of their proposal was to demonstrate how other alkenes might give rise to some of the same chemiluminescent species as are observed in the O_3–ethene reaction. For example, chemiluminescence from H_2CO ($^1A''$) was observed in all the O_3–alkene systems studied by Finlayson et al.,[32] and it was not affected by the presence of O_2. Wadt and Goddard[3] argued that the most likely mechanism for H_2CO ($^1A''$) production in the ozone–ethene system is the attack by O_3 on the planar $^1A'(4\pi)$ state of H_2COO.

$$H_2COO \; [^1A'(4\pi)] + O_3 \rightarrow$$
$$H_2CO \; (^1A'') + 2O_2 \qquad \Delta H \simeq -113 \text{ kJ mol}^{-1} \quad (42)$$

The reaction is sufficiently exothermic so that the H_2CO ($^1A''$) is probably produced with at least 29 kJ mol^{-1} of vibrational excitation, in which case it can dissociate to $H + HCO$, thereby

providing a source of H atoms and, therefore, a source of OH Meinel bands via $H + O_3 \rightarrow OH^\dagger + O_2$. The isomerization and subsequent decomposition of H_2COO also provides a source of H atoms and therefore OH†.

It is clear that for the alkenes studied by Finlayson et al.,[32] the sequence of reactions 14 and 17, and by analogy (18) and (21), do provide a source of H_2COO and hence of H_2CO ($^1A''$) and OH ($X^2\Pi_i)_{v' \leq 9}$.[42] Thus, while ethene, propene, 1-butene, and 2-methylpropene can provide H_2COO directly via the primary Criegee split (reaction 4), the alkenes 2-methylpropene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene can provide H_2COO via reaction 17, and the alkenes propene and *cis*- and *trans*-2-butene can provide H_2COO via reaction 21. Consequently, the observations by Finlayson et al.[32] of OH and H_2CO chemiluminescence from the reaction of O_3 with these alkenes in the presence and absence of O_2 can be explained by reactions of the primary Criegee intermediates, as outlined above. And, as was discussed in section D, such reactions [(15)–(17) and (19)–(21)] represent very minor processes in the O_3–alkene systems.

(ii) C_m Alkene Products. C_m alkenes have been reported as products of the reaction of O_3 with a variety of C_n alkenes.[12,43] However, this discussion will be restricted to the production of C_2H_4 ($\sim 0.02-0.04$ mol/mol of alkene consumed) by the reaction of O_3 with 1-butene[12,43] or 2-pentene[12,43] (also see Table VI) or 2-ethyl-1-butene (see Table VIII). One possible source of C_2H_4 is via its unimolecular elimination from the corresponding primary Criegee intermediate, subsequent to its rearrangement to an excited alkanoic acid derivative[24] (reactions 43–46), where R' = H
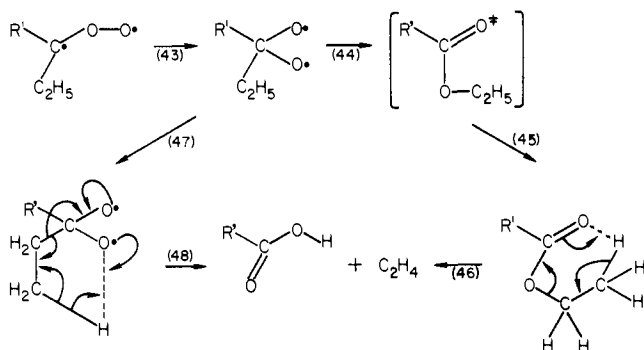
for 1-butene and 2-pentene and C_2H_5 for 2-ethyl-1-butene. Peaks corresponding to the expected acid derivatives were observed at m/e 46 for 2-pentene (see Table VI) and m/e 74 for 2-ethyl-1-butene (see Table VIII). Additional support for this plausible mechanism comes from the work of Ausloos[44] and Wijnen[45] on the gas-phase photolysis of alkyl esters. They demonstrated that C_2H_4 was a primary product arising from the intramolecular rearrangement and decomposition of both ethyl propanoate[44,45] and ethyl methanoate,[44] which correspond respectively to the Criegee intermediates expected from 2-ethyl-1-butene and 2-pentene (or 1-butene).

The above mechanism [(43)–(46)] necessitates the migration of bulky alkyl groups to form an actual "hot" acid intermediate, which although possible, seems less probable than a radical fragmentation process whereby the migrating bulky alkyl group falls off during its attempted rearrangement, thus forming a radical pair such as $(R'C(=O)—O\cdot + C_2H_5\cdot)$ or $(R'C(=O)\cdot + C_2H_5O\cdot)$. Consequently, we propose the reaction sequence (43), (47), and (48) as the most probable source of the molecular products $R'C(O)OH$ and C_2H_4.

Vrbaski and Cvetanovic[43] proposed instead an H-atom migration within the primary Criegee intermediate followed by

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(40) H. E. Radford, *Chem. Phys. Lett.*, **71**, 195 (1980).

(41) A. Horowitz, F. Su, and J. G. Calvert, *Int. J. Chem. Kinet.*, **10**, 1099 (1978).

(43) T. Vrbaski and R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1063 (1960).

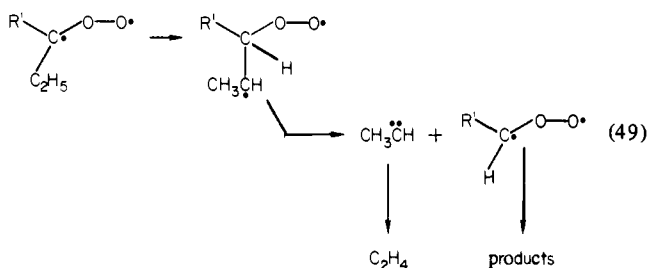(44) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).

(45) M. H. J. Wijnen, *J. Am. Chem. Soc.*, **82**, 3034 (1960).

elimination of $CH_3\ddot{C}H$ and the corresponding Criegee fragment.

However, the newly formed Criegee intermediate $R'\dot{C}(H)OO\cdot$ would be expected to rearrange and decompose, without significant stabilization to the corresponding acid product.[24]

It is clear that the mechanisms involved in the formation of "anomalous" products such as C_m alkenes are still poorly understood but do suggest the involvement of intramolecular rearrangement processes such as those outlined here. For example, alkenes could also be formed from the decomposition of the hot epoxyalkane[46] formed in the ozone-alkene reaction.

Conclusions

The products of gas-phase ozone-alkene reactions are characteristic of (i) a primary Criegee split (reaction 4) to a C_m oxoalkane and a Criegee intermediate, (ii) competing loss processes for the Criegee intermediates, viz., unimolecular decomposition vs. reactions such as secondary ozonide formation etc., and (iii) secondary alkene chemistry involving OH and the other free-radical products which are formed by the unimolecular decomposition of the Criegee intermediates. The alkanoic acids appear to be products of a variety of slow reactions involving oxoalkanes which are produced in the O_3-alkene systems. The C_n oxoalkanes and C_n epoxyalkanes appear to be formed via epoxidation of the C_nH_{2n} alkene primarily by O_3. While the production of C_n ketenes and C_n oxoalkenes is probably initiated by OH addition to the alkene, the C_m ketenes appear to be Criegee rearrangement products. Thus, for different O_3-alkene reactions, the same compound or classes of compounds (e.g., ketenes) may arise from very different reaction mechanisms, thereby complicating the unraveling of the overall gas-phase O_3-alkene reaction mechanism.

The secondary OH-alkene-O_2 reactions account for a significant fraction of the alkene consumed and lead to characteristic products such as dioxoalkanes, acyloins, and alkanediols. The OH radicals which initiate these reactions can be produced directly from the unimolecular decomposition of a Criegee intermediate in reactions such as (3d) or its homologue, reaction 50. Sub-

$$CH_3\dot{C}HOO\cdot \rightarrow [CH_3C(O)OH]^* \rightarrow OH + CH_3C(O) \quad (50)$$

$$\rightarrow CH_3 + COOH \quad (51)$$
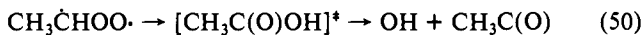
sequent reactions of hydrogen atoms, alkyl radicals, and other primary free-radical decomposition products of Criegee intermediates [e.g., CH_3 from (51)] also can lead to OH or HO_2. Reactions of radicals with ozone may be an additional OH source, e.g.

$$CH_3 + O_3 \rightarrow OH + H_2COO \quad (52)$$
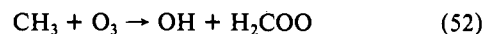
This reaction is of considerable interest as a possible new source of the Criegee intermediate.[47] Reactions such as (52), however, can only be important under experimental conditions such as used here ($\gtrsim 4\%$ O_3 in O_2, total pressure $\lesssim 4$–8 torr), where the consumption of CH_3 by reaction with O_3 is competitive with the consumption of CH_3 by reaction with O_2. Thus, for example, on the basis of a recent determination of the rate constant for the $CH_3 + O_3$ reaction,[47] the rates of reactions $CH_3 + O_3$ and $CH_3 + O_2$ are about equal under our reaction conditions. Under atmospheric conditions, however, the $CH_3 + O_3$ reaction would be unimportant.

As we discuss elsewhere,[24] relative rates of reactions participating in O_3-alkene systems are very significantly altered by reaction conditions, thereby influencing observed product distributions and assumed mechanisms. For example, high aldehyde concentrations will tend to stabilize the initially formed excited Criegee intermediate,[24] thereby reducing the free-radical activity of the system while encouraging secondary ozonide formation. Increasing the total pressure will also affect the product distribution because of third-body effects. However, these will not only alter the secondary radical chemistry (e.g., $H + O_2 \xrightarrow{M} HO_2$ followed by $HO_2 + O_3 \rightarrow OH + 2O_2$) but also affect to varying degrees the stabilization of the initially formed excited Criegee intermediate and consequently the free-radical activity of the O_3-alkene system. Hence, in order to unravel the *complete* gas-phase reaction mechanism, one must determine the product distributions as a function of total pressure and reactant concentrations.

The extremely complex secondary chemistry found in ozone-alkene reactions is a consequence of the unimolecular decomposition of Criegee intermediates. The chemistry of the Criegee intermediate remains the single most important problem area in understanding the gas-phase mechanism of ozone-alkene reactions. It is interesting to note, therefore, that it has been suggested that the Criegee intermediate may also participate in combustion[48] and in the photooxidation of aldehydes.[49]

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