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# The gas phase ozonolysis of tetramethylethylene

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THE GAS PHASE OZONOLYSIS OF TETRAMETHYLETHYLENE

by

Catherine A. Rusik

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Submitted in partial fulfillment  
of the requirements for  
Honors in the Department of Chemistry

UNION COLLEGE

March, 1982

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# ABSTRACT

RUSIK, CATHERINE A. The Gas Phase Ozonolysis of Tetramethylethylene. Department of Chemistry March 1982.

The gas phase reaction between ozone and olefins is thought to proceed via an oxy-peroxy biradical intermediate, which may undergo cleavage or a variety of hydrogen abstractions. The validity of this biradical mechanism is investigated in a study of the products and stoichiometry of the gas phase ozonolysis of tetramethylethylene. Various pathways in the ozonolysis mechanism for this olefin are compared thermochemically to assess the relative favorability of the reaction possibilities of the biradical intermediate.

Experimentally, olefin-rich and ozone rich reaction conditions are studied in the concentration range 10-800 ppm, using gas chromatography. The concentration of ozone present is determined by a spectrometric buffered KI method. Acetone is identified as a major product in the ozonolysis of tetramethylethylene. The stoichiometry of the reaction is found to be a function of initial reactant concentrations in both olefin-rich and ozone-rich conditions. Acetone yields exhibit direct concentration dependence in the presence of excess olefin and inverse dependence in the presence of excess ozone. In addition, the yield of acetone

is overall much lower in an ozone-rich environment than in the olefin-rich case. The possible existence of additional pathways in the biradical ozonolysis mechanism is suggested in terms of these observations. Results of this study are compared with previous work at higher concentrations, and the modelling of atmospheric ozonolysis reactions is considered.

#### ACKNOWLEDGEMENTS

Several people have played an important role in the completion of this project. I extend thanks to Professor Leslie Hull for his patience, encouragement, and guidance; also to Marabeth Soltis for her constant support. Finally, I would like to thank my family for their interest and concern. This work is dedicated to these people with great appreciation.

"Enthusiasm is the electricity of life. How do you get it? You act enthusiastic until you make it a habit. Enthusiasm is natural; it is being alive, taking the initiative, seeing the importance of what you do, giving it dignity and making what you do important to yourself and to others."

- Gordon Parks

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## INTRODUCTION

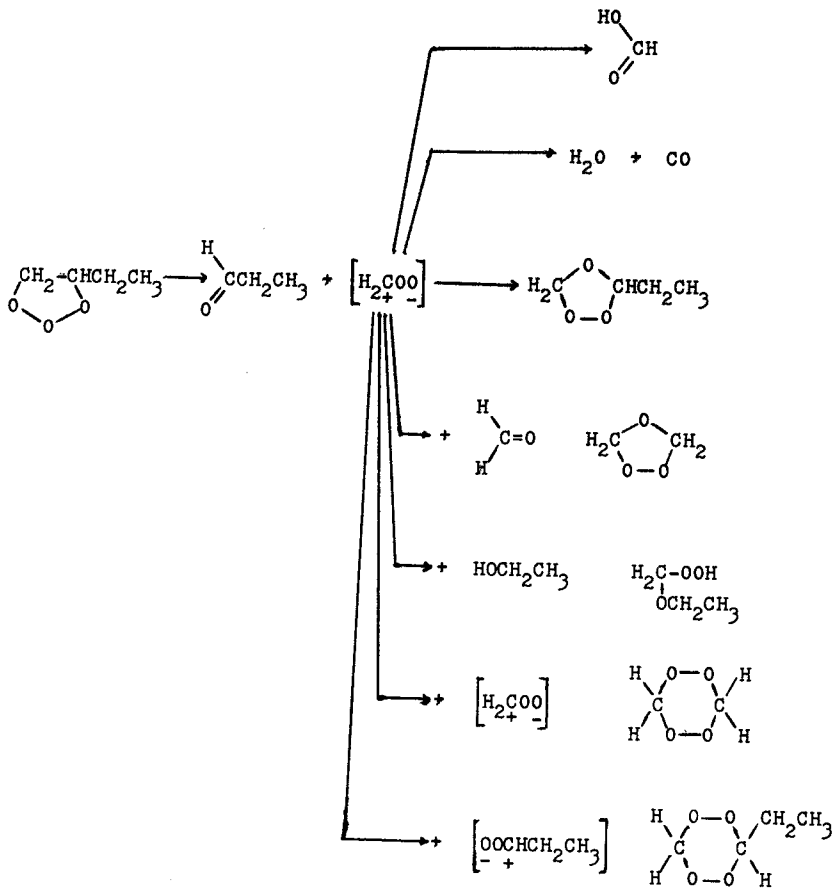
Ozone-olefin reactions are known to give a variety of very complex product mixtures. Since about 1950, considerable efforts have been made in an attempt to better understand the mechanism of ozonolysis. Early work in the liquid phase resulted in Criegee's proposal,<sup>1</sup> suggesting the initial formation of a 1,2,3-trioxetane five-membered ring (molozonide). The molozonide decomposes to carbonyl and zwitterion products which can then react further. One reaction possibility involves recombination of the molozonide fragments to form the monomeric secondary ozonide, a 1,2,4-trioxetane. This species has been identified as the major product in condensed-phase work.<sup>2-9</sup> The observed complexity of the final product mixture is explained by subsequent rearrangements, additions, and dimerizations involving the zwitterions formed. The Criegee mechanism for 1-butene is summarized in Scheme 1.

The Criegee ozonolysis mechanism was originally assumed to be applicable not only to the reactions in solution that it was based upon, but also to gaseous ozone-olefin reactions. However, experimental work in the gas phase produced results that were increasingly difficult to rationalize in terms of the Criegee mechanism.<sup>10-15</sup> In 1973, O'Neal and

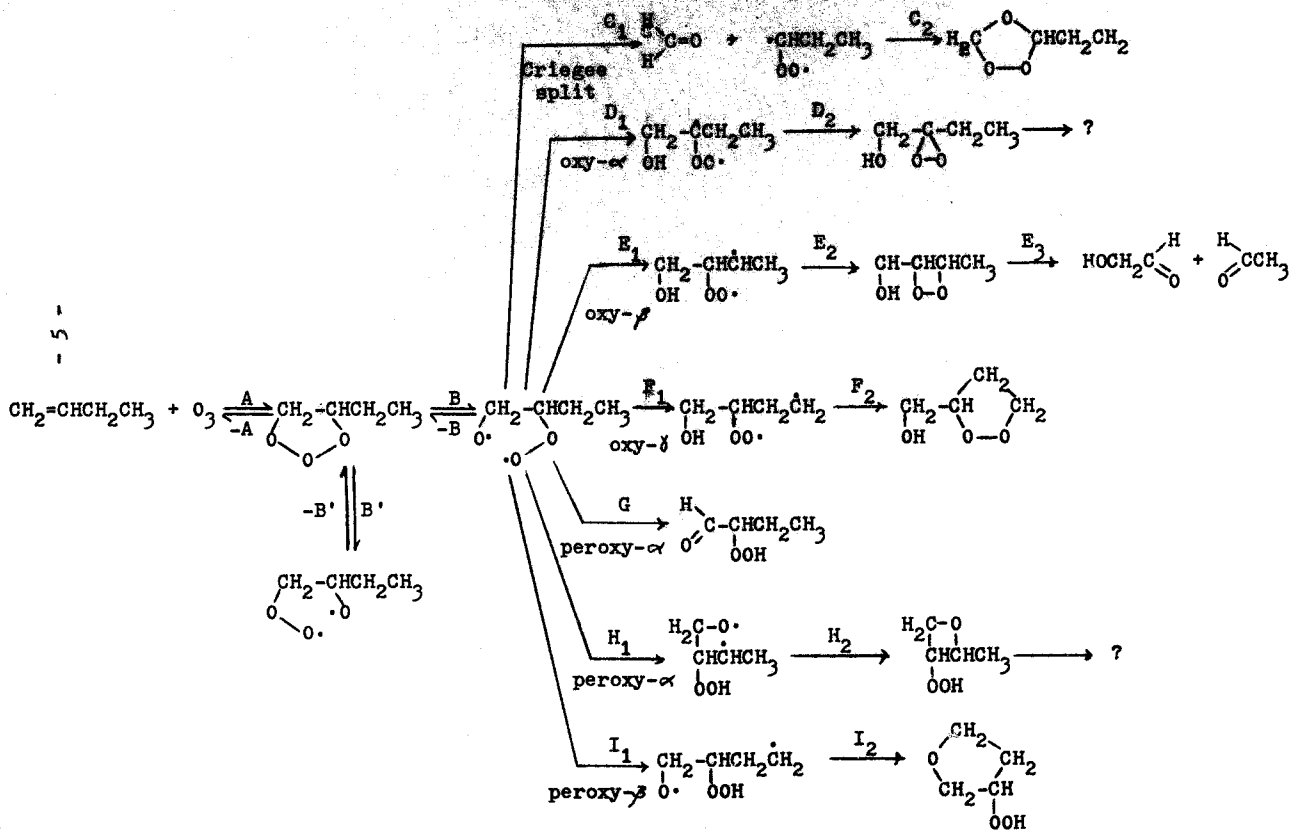
Blumstein<sup>16</sup> proposed an alternative mechanism for gas-phase ozonolysis. Rather than decomposition of the initial ozonide (molozone) to carbonyl and zwitterion products, the O'Neal-Blumstein mechanism (Scheme 2) postulates a ring-opening reaction (path B), forming a biradical intermediate which can react in a variety of ways. Either O-O bond in the molozone bridge may break, so unsymmetric olefins produce two biradical forms. Each biradical may undergo bond fission (path C) which yields the typical Criegee products. In addition, various intramolecular hydrogen abstractions (from  $\alpha$ ,  $\beta$ , and  $\gamma$  carbons) are possible for both the oxy and peroxy radical centers (paths D-I and K-P).

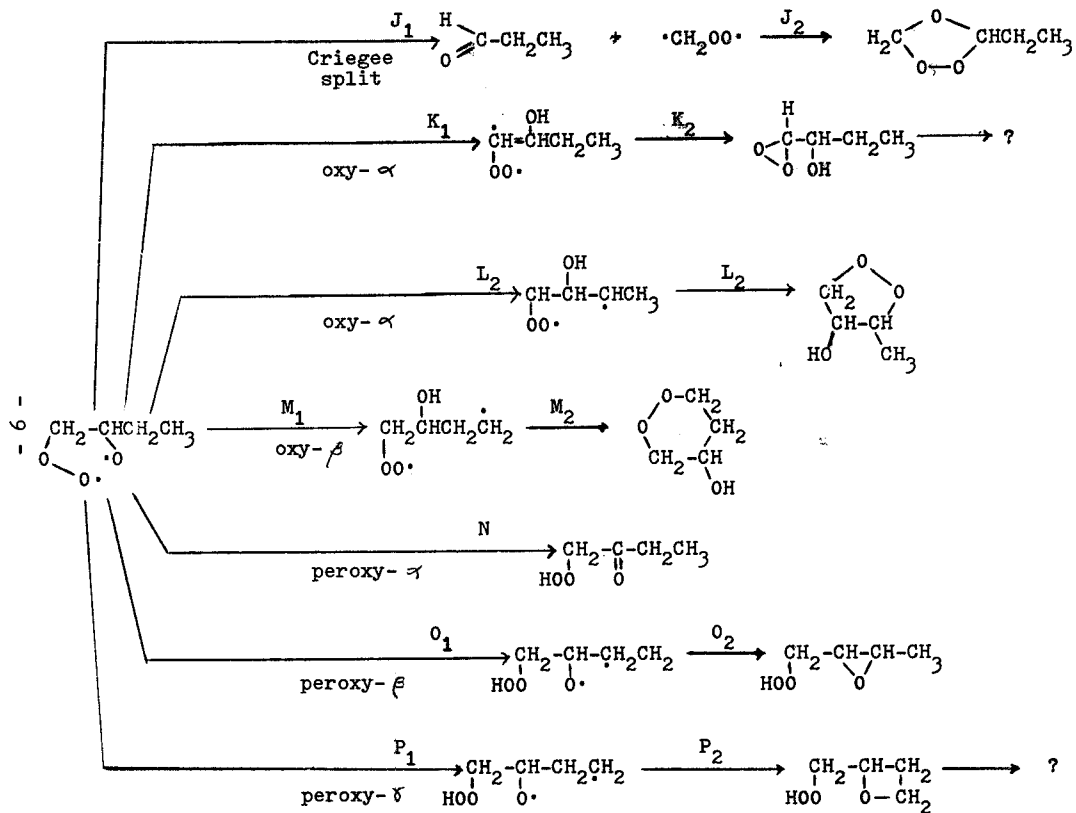
The O'Neal-Blumstein mechanism is generally accepted as the more reasonable explanation of gas-phase ozonolysis, as it not only provides a plausible interpretation of the variety and relative yields of products, but also accounts for a number of unusual experimental observations which are unexplainable in terms of the Criegee mechanism. One example is the reported fluorescence of ozone-olefin reaction mixtures at low total pressures.<sup>12,13,15,16</sup> Pathway E involves the formation of a four-membered 1,2-dioxetane ring. Dioxetanes are rather unstable at room temperature and are known to decompose to aldehydes and ketones with light emission.<sup>17,18</sup> Thus the observed fluorescence supports the choice of the O'Neal-Blumstein mechanism to describe gas-phase ozonolysis.





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# THERMOCHEMICAL CONSIDERATIONS

Before attempting to rationalize ozonolysis products in terms of the O'Neal-Blumstein mechanism, it is worthwhile to consider the thermochemistry of the various reaction pathways. Comparison of heats of reaction can give information about the relative favorability of each possible pathway, which in turn is used to predict the probable composition of experimental product mixtures.

The  $O_3 + 1$ -butene reaction was chosen as a model. These calculations are similar in form to those of O'Neal and Blumstein. The heat of reaction of each step is calculated from the heats of formation of the products and reactants involved:

$$A + B \xrightarrow{\text{rxn.}} C + D$$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_f^{\circ} (\text{products}) - \Delta H_f^{\circ} (\text{reactants})$$

$$= \Delta H_{f,C}^{\circ} + \Delta H_{f,D}^{\circ} - \Delta H_{f,A}^{\circ} - \Delta H_{f,B}^{\circ}$$

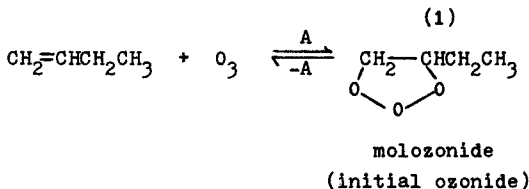
Only for the simplest compounds ( $O_3$ , formaldehyde, and 1-butene) are the heats of formation directly available from tables. The required  $\Delta H_f^{\circ}$  values for more complex species are obtained by Benson's method of group additivities.<sup>19</sup> The heat of formation of a species is approximated as the sum of the contributions from the individual atoms and bonds that it contains. The species is considered as a collection of groups of atoms, each contributing a specific amount to

the total  $\Delta H_f^\circ$ . A group is defined as an atom and its ligands. Additive heats of formation of component groups are found in Benson's tables. Occasionally approximations must be made for additive values not listed. Those estimates were made in a systematic way so that the following method can be applied to the analysis of other ozone-alkene reactions.

### Thermochemistry of 1-Butene

#### A. Molozonide Formation

The initial step in the O'Neal-Blumstein ozonolysis mechanism is the addition of ozone to the olefin, forming the molozonide:

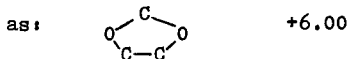


The heat of formation of the molozonide is calculated via Benson's additivity values.<sup>19</sup> A correction must be made for molozonide ring strain. The effect of strain in a five-membered 1,2,3-trioxetane ring is not available from tables. According to Benson, heterocyclic ring strain may be approximated by using the strain value for a corresponding hydrocarbon ring. Therefore, the value is estimated to be the

same as that of a similar five-membered 1,3-dioxocyclopentane ring.

Additive $\Delta H_f^\circ$ , (1):	C-(O)(C)(H) <sub>2</sub>	-8.1
	C-(O)(C) <sub>2</sub> (H)	-7.2
	2( O-(O)(C) )	2(-4.5)
	O-(O) <sub>2</sub>	+19.0
	C-(C) <sub>2</sub> (H) <sub>2</sub>	-4.93
	C-(C)(H) <sub>3</sub>	-10.20

ring strain, estimated



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$$-14.4 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_f^\circ (\text{O}_3) = 34.8 \frac{\text{kcal}}{\text{mole}}^{20}$$

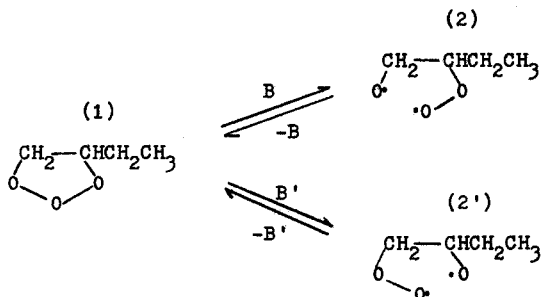
$$\Delta H_f^\circ (\text{1-butene}) = -0.2 \frac{\text{kcal}}{\text{mole}}^{21}$$

The heats of formation of the reactants and products are then used to find the heat of reaction for molozonide formation:

$$\begin{aligned} \Delta H_A^\circ &= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ &= \Delta H_f^\circ, (1) - \Delta H_f^\circ (\text{1-butene}) - \Delta H_f^\circ (\text{O}_3) \\ &= -14.4 - (-0.2) - 34.8 = -49.0 \frac{\text{kcal}}{\text{mole}} \end{aligned}$$

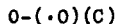
### B. Oxy-peroxy Biradical Formation

The molozonide undergoes reversible ring opening, yielding an oxy-peroxy biradical. Either O-O bond may cleave in this equilibrium process, so two biradical species can be produced.



To calculate the additive heat of formation of the oxy-peroxy biradical, additivity values of three groups not listed in Benson's tables are required. One value is approximated as that of a non-radical group, and the other two values are obtained by calculation, using Benson's table of heats of formation for gas-phase organic free radicals.

Radical groups for which additivity values are required:



The additive  $\Delta H_F^\circ$  of  $O-(\cdot O)(C)$  is approximated as that of  $O-(O)(C)$ . This is reasonable because the unpaired electron is located on a ligand of the central atom, rather than on the central atom. Since the forces between atoms are very short-range, the  $\alpha$ -effect of the unpaired electron is assumed to be small.

The approximated value for  $O-(\cdot O)(C)$  and a tabulated value for the heat of formation of the methyl peroxy radical<sup>19</sup> are used to calculate the additive  $\Delta H_F^\circ$  of  $\cdot O-(O)$ :

$$\Delta H_F^\circ (CH_3OO\cdot) = +6.7 \frac{\text{kcal}}{\text{mole}}$$

$$\text{Additive } \Delta H_F^\circ (CH_3OO\cdot): \quad C-(O)(H)_3 \quad -10.08$$

$$\begin{array}{lcl} \text{approximated as } \longrightarrow O-(\cdot O)(C) & & -4.5 \\ O-(O)(C) & & \end{array}$$

$$\cdot O-(O) \quad x$$

$$\Delta H_F^\circ (CH_3OO\cdot) = \text{known additive } \Delta H_F^\circ \text{'s} + x$$

$$+6.7 = -14.58 + x$$

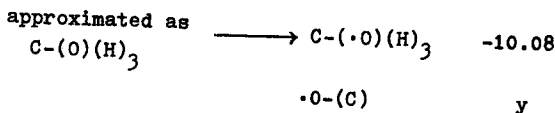
$$x = +21.3 \frac{\text{kcal}}{\text{mole}} = \text{Additive } \Delta H_F^\circ \cdot O-(O)$$

Likewise, the additive  $\Delta H_F^\circ$  of the group  $\cdot O-(C)$  is found using the heat of formation of the methoxy radical.<sup>19</sup> In this calculation, the group additivity of  $C-(\cdot O)(H)_3$  is approximated as that of  $C-(O)(H)_3$ . Again, the effect of

the unpaired electron  $\propto$  to the central atom is assumed to be small.

$$\Delta H_f^\circ (\text{CH}_3\text{O}\cdot) = +3.5 \frac{\text{kcal}}{\text{mole}}$$

$$\text{Additive } \Delta H_f^\circ (\text{CH}_3\text{O}\cdot):$$



$$\Delta H_f^\circ (\text{CH}_3\text{O}\cdot) = \text{known additive } \Delta H_f^\circ + y$$

$$+3.5 = -10.08 + y$$

$$y = +13.6 \frac{\text{kcal}}{\text{mole}} = \text{Additive } \Delta H_f^\circ \cdot\text{O}-(\text{C})$$

Now that the required group additivity values are known, the additive heat of formation of the oxy-peroxy biradical ( $\Delta H_{f,(2)}^\circ$ ) can be calculated:

$$\text{Additive } \Delta H_{f,(2)}^\circ: \quad \text{C}-(\cdot\text{O})(\text{C})(\text{H})_2 \quad +6.1^{22}$$

$$\text{calculated } \longrightarrow \cdot\text{O}-(\text{C}) \quad +13.6$$

$$\text{C}-(\text{O})(\text{C})_2(\text{H}) \quad -7.2$$

approximated as

$$\text{O}-(\text{O})(\text{C}) \longrightarrow \text{O}-(\cdot\text{O})(\text{C}) \quad -4.5$$

$$\text{calculated } \longrightarrow \cdot\text{O}-(\text{O}) \quad +21.3$$

$$\text{C}-(\text{C})_2(\text{H})_2 \quad -4.93$$

$$\text{C}-(\text{C})(\text{H})_3 \quad -10.20$$

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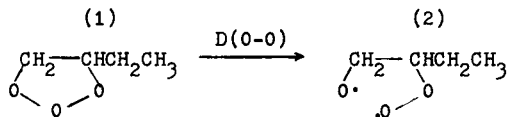

$$+14.2 \frac{\text{kcal}}{\text{mole}}$$

Additive  $\Delta H_f^\circ$  values are listed for only one of the biradicals, labeled (2). Additive  $\Delta H_{f,(2)}^\circ$ , in which the other O-O bond is broken, is the same as  $\Delta H_{f,(2)}^\circ$ , since Benson additivities consider only  $\alpha$ -effects and not  $\beta$ -effects.

The reaction heat of biradical formation is found from the heats of formation of the species involved:

$$\begin{aligned}\Delta H_B^\circ &= \Delta H_B^\circ = \Delta H_{f,(2)}^\circ - \Delta H_{f,(1)}^\circ = +14.2 - (-14.4) \\ &= +28.6 \frac{\text{kcal}}{\text{mole}}\end{aligned}$$

The biradical formation reaction is an O-O bond dissociation; therefore  $\Delta H_B^\circ = D(0-0)$ .

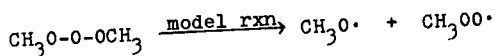


$$\begin{aligned}D(0-0) &= \Delta H_{f,(2)}^\circ - \Delta H_{f,(1)}^\circ = +14.2 - (-14.2) \\ &= +28.6 \frac{\text{kcal}}{\text{mole}}\end{aligned}$$

This O-O bond dissociation energy is comparable to values for organic D(0-0), which range 30-36  $\frac{\text{kcal}}{\text{mole}}$ . However, calculations by O'Neal and Blumstein resulted in a markedly different D(0-0) value of about 14  $\frac{\text{kcal}}{\text{mole}}$ . It appears that the O'Neal-Blumstein value for the heat of formation of the biradical is based on a model O-O bond dissociation reaction. This is an alternative method, rather than approx-

imating the additive heat of formation for  $O-(\cdot O)(C)$  and calculating the unknown additivities from tabulated values for organic radicals.

The model dissociation reaction involves species for which heats of formation are available. The  $O-O$  bond dissociation energy for the formation of the oxy-peroxy biradical is estimated by correcting the calculated dissociation energy of the model reaction for the added effect of strain relief, due to ring-opening.



Additive  $\Delta H_f^\circ (CH_3O-O-OCH_3):$

$2(C-H)_3(O)$	$2(-10.08)$
$2(O-(C)(O))$	$2(-4.5)$
$O-(O)_2$	$+19.0$

---


$$-10.2 \frac{\text{kcal}}{\text{mole}}$$

Tabulated heats of formation of organic radicals:

$$\Delta H_f^\circ (CH_3O\cdot) = +3.5 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_f^\circ (CH_3OO\cdot) = +6.7 \frac{\text{kcal}}{\text{mole}}$$

$$\begin{aligned} \Delta H_{\text{model rxn}}^\circ &= \Delta H_f^\circ (CH_3O\cdot) + \Delta H_f^\circ (CH_3OO\cdot) - \Delta H_f^\circ (CH_3O-O-OCH_3) \\ &= +3.5 + 6.7 - (-10.2) \\ &= +20.4 \frac{\text{kcal}}{\text{mole}} = D(O-O) \end{aligned}$$



$$\begin{aligned}\Delta H_B^{\circ} &= \Delta H_{\text{model rxn}}^{\circ} - \text{ring strain relieved} \\ &= -20.4 - 6.00 = 14.4 \frac{\text{kcal}}{\text{mole}}\end{aligned}$$

Once the heat of reaction is known, the heat of formation of the oxy-peroxy biradical can be calculated:

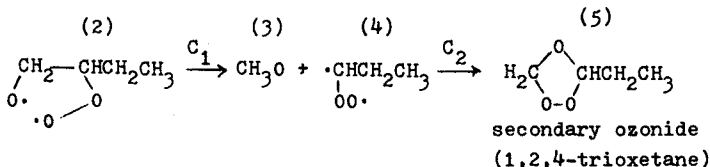
$$\begin{aligned}\Delta H_B^{\circ} &= \Delta H_{f,(2)}^{\circ} - \Delta H_{f,(1)}^{\circ} \\ \Delta H_{f,(2)}^{\circ} &= \Delta H_B^{\circ} + \Delta H_{f,(1)}^{\circ} = +14.4 + (-14.4) = 0 \frac{\text{kcal}}{\text{mole}}\end{aligned}$$

This suggests that O'Neal and Blumstein used an estimated  $\Delta H_f^{\circ}$  value of zero for the biradical. The O'Neal-Blumstein heat of formation of the oxy-peroxy biradical differs significantly from the value obtained by approximating group additivities. In calculations that involve  $\Delta H_{f,(2)}^{\circ}$ , both the value calculated via approximation of radical group values and the apparent O'Neal-Blumstein value were used. Then the results obtained with each were compared.

### C. Further Reactions of the Oxy-peroxy Biradical

#### 1. Criegee Split

Bond fission may occur, resulting in secondary ozonides as predicted by the Criegee ozonolysis mechanism.



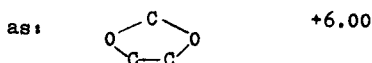
The heat of formation of the biradical has already been calculated, and that of formaldehyde is directly available:

$$\begin{aligned}\Delta H_{f,(2)}^{\circ} &= 0 \text{ (O'Neal-Blumstein method)} \\ &= +14.2 \text{ (by approximation)}\end{aligned}$$

$$\Delta H_{f,(3)}^{\circ} = -27.70 \frac{\text{kcal}}{\text{mole}}^{23}$$

Additive	$H_{f,(5)}^{\circ}$	$C-(O)_2(H)_2$	-16.1
		$O-(C)_2$	-23.2
		$2(O-(O)(C))$	$2(-4.5)$
		$C-(O)_2(C)(H)$	-16.3
		$C-(C)_2(H)_2$	-4.93
		$C-(C)(H)_3$	-10.20

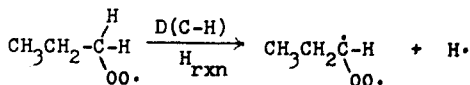
ring strain, estimated



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$$-73.7 \frac{\text{kcal}}{\text{mole}}$$

The heat of formation of species (4) is not directly available, so it is calculated using the method of Wadt and Goddard.<sup>24</sup>  $\Delta H_{f,(4)}^{\circ}$  is estimated by consideration of a dissociation reaction involving species for which heat of formation data is available:



$$D(C-H) = \Delta H_{rxn} = \Delta H_F^{\circ}(CH_3CH_2\dot{C}HOO\cdot) + \Delta H_F^{\circ}(H\cdot) - \Delta H_F^{\circ}(CH_3CH_2CH_2OO\cdot)$$

The expression is then solved for the unknown heat of formation,  $\Delta H_F^{\circ}(4)$ :

$$\Delta H_F^{\circ}(4) = \Delta H_F^{\circ}(CH_3CH_2\dot{C}HOO\cdot) = D(C-H) + \Delta H_F^{\circ}(CH_3CH_2CH_2OO\cdot) - \Delta H_F^{\circ}(H\cdot)$$

The heat of formation of a hydrogen atom is available in Benson's tables:

$$\Delta H_F^{\circ}(H\cdot) = 52.1 \frac{\text{kcal}}{\text{mole}}$$

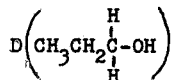
$\Delta H_F^{\circ}(CH_3CH_2CH_2OO\cdot)$  is calculated directly via additive heats of formation:

Additive  $\Delta H_F^{\circ}(CH_3CH_2CH_2OO\cdot)$ :

	C-(C)(H) <sub>3</sub>	-10.20
	C-(C) <sub>2</sub> (H) <sub>2</sub>	-4.93
	C-(O)(C)(H) <sub>2</sub>	-8.1
approximated as		
0-(O)(C)	→ 0-(·O)(C)	-4.5
calculated →	0-(O)	+21.3
		<hr/>
		-6.4 $\frac{\text{kcal}}{\text{mole}}$

$$\Delta H_F^{\circ}(CH_3CH_2\dot{C}HOO\cdot) = D(C-H) + \Delta H_F^{\circ}(CH_3CH_2CH_2OO\cdot) + \Delta H_F^{\circ}(H\cdot)$$

Now only  $D(C-H)$  is required to find  $\Delta H_F^{\circ}(4)$ . The C-H bond strength should be comparable to that in propanol:



The propanol C-H bond strength is estimated by using an alkyl C-H bond strength and correcting for the stabilization of the CO- $\pi$  bond.

$$D\left(\text{CH}_3\overset{\text{H}}{\text{CH}}\text{CH}_3\right) = 95 \frac{\text{kcal}}{\text{mole}}^{25}$$

The stabilization of the three-electron CO- $\pi$  bond is estimated at  $4 \frac{\text{kcal}}{\text{mole}}$ ,<sup>24</sup> so, by analogy:

$$D\left(\text{CH}_3\text{CH}_2\overset{\text{H}}{\text{C}}\text{HOO}\cdot\right) = 91 \frac{\text{kcal}}{\text{mole}}$$

Now the required heat of formation can be calculated:

$$\begin{aligned}\Delta H_{f,(4)}^{\circ} &= \Delta H_f^{\circ}(\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOO}\cdot) = D(\text{C-H}) - \Delta H_f^{\circ}(\text{H}\cdot) + \Delta H_f^{\circ}(\text{CH}_3\text{CH}_2\text{CH}_2\text{OO}\cdot) \\ &= 91 - 52.1 + (-6.4) = +32.5 \frac{\text{kcal}}{\text{mole}}\end{aligned}$$

Using the heats of formation of the reactants and products, the reaction heat of each step in the Criegee split pathway is calculated. (Both values for the biradical heat of formation are given.)

$$\Delta H_{C_1}^{\circ} = \Delta H_{f,(3)}^{\circ} + \Delta H_{f,(4)}^{\circ} - \Delta H_{f,(2)}^{\circ}$$

The O'Neal-Blumstein value for  $\Delta H_{f,(2)}^{\circ} = 0 \frac{\text{kcal}}{\text{mole}}$ ,

$$\Delta H_{C_1}^{\circ} = -27.70 + 32.5 - 0 = +4.8 \frac{\text{kcal}}{\text{mole}}$$

The value of  $\Delta H_{f,(2)}^{\circ} = +14.2 \frac{\text{kcal}}{\text{mole}}$ , found by approximating additive  $\Delta H_f^{\circ}$  values:

$$\Delta H_{C_1}^{\circ} = -27.70 + 32.5 - 14.2 = -9.4 \frac{\text{kcal}}{\text{mole}}$$

$$\begin{aligned} \Delta H_{C_2}^{\circ} &= \Delta H_{f,(5)}^{\circ} - \Delta H_{f,(3)}^{\circ} - \Delta H_{f,(4)}^{\circ} \\ &= -73.7 - (-27.70) - (+32.5) = -78.5 \frac{\text{kcal}}{\text{mole}} \end{aligned}$$

The two methods of calculating  $\Delta H_{f,(2)}^{\circ}$  give different results for the Criegee split reaction. The O'Neal-Blumstein value, based on a model 0-0 bond dissociation reaction, gives a slightly endothermic ( $+4.8 \frac{\text{kcal}}{\text{mole}}$ ) and therefore less favorable heat of reaction for the Criegee split. The method of approximating additive heats of formation of radical groups gives a  $\Delta H_{f,(2)}^{\circ}$  value that makes the Criegee split reaction exothermic ( $-9.9 \frac{\text{kcal}}{\text{mole}}$ ) and therefore quite favorable.

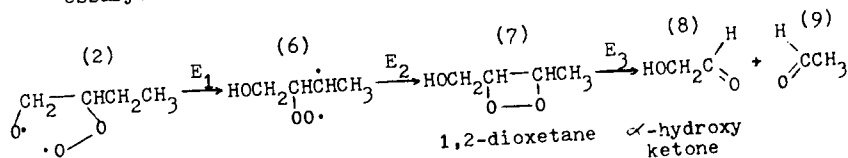
In addition to bond fission, O'Neal and Blumstein propose a variety of hydrogen abstraction pathways involving both the oxy and peroxy portions of the biradical. Each hydrogen abstraction results in another biradical species which may rearrange or ring-close. In some cases (paths E, H, and P) ring closure produces four-membered cyclic units, which are quite strained and probably undergo cleavage to carbonyl products. Several stable five- and six- membered heterocyclic products are predicted (paths F, I, L, and M)

Epoxides and  $\alpha$ -keto hydroperoxides are also possible (paths G, H, and O).


## 2. Oxy- $\beta$ -hydrogen Abstraction

This abstraction pathway results in initial formation of a four-membered ring, which subsequently cleaves<sup>26</sup> and possibly fluoresces.<sup>17,18</sup> The final products are an  $\alpha$ -hydroxy ketone and an "unusual" aldehyde; that is an aldehyde which is not predicted by the Criegee mechanism. Both the fluorescence and the unexpected aldehydes have been observed experimentally, which supports the choice of the O'Neal-Blumstein mechanism to describe gas phase ozonolysis.

The required heats of formation are found via additivity. Two approximations for radical group values are necessary.



Additive $\Delta H_f^\circ, (6)'$	O-(C)(H)	-37.9
	O-(O)(C)(H) <sub>2</sub>	-8.1
approximated as	C-(O)(C) <sub>2</sub> (H) $\rightarrow$ C-(O)(·C)(C)(H)	-7.2
approximated as	O-(·O)(C) $\rightarrow$ O-(·O)(C)	-4.5
previously calculated $\rightarrow$	·O-(O)	+21.3

$\cdot\text{C}-(\text{C})_2(\text{H})$	+37.45
$\text{C}-(\cdot\text{C})(\text{H})_3$	-10.08
	<hr/>
	-9.0 $\frac{\text{kcal}}{\text{mole}}$
Additive $\Delta H_{\text{f}}^{\circ}(7)$ : $\text{O}-(\text{C})(\text{H})$	-37.9
$\text{C}-(\text{O})(\text{C})(\text{H})_2$	-8.1
$2(\text{C}-(\text{O})(\text{C})_2(\text{H}))$	$2(-7.2)$
$2(\text{O}-(\text{O})(\text{C}))$	$2(-4.5)$
$\text{C}-(\text{C})(\text{H})_3$	-10.20
ring strain, estimated	
as: 	+25.7
	<hr/>
	-53.9 $\frac{\text{kcal}}{\text{mole}}$
Additive $\Delta H_{\text{f}}^{\circ}(8)$ : $\text{O}-(\text{C})(\text{H})$	-37.9
approximated as $\text{C}-(\text{O})(\text{CO})(\text{H})_2$	-8.1
$\text{C}-(\text{O})(\text{C})(\text{H})_2$	-29.1
$\text{CO}-(\text{C})(\text{H})$	-29.1
	<hr/>
	-75.1 $\frac{\text{kcal}}{\text{mole}}$
Additive $\Delta H_{\text{f}}^{\circ}(9)$ : $\text{CO}-(\text{C})(\text{H})$	-29.1
$\text{C}-(\text{CO})(\text{H})_3$	-10.20
	<hr/>
	-39.3 $\frac{\text{kcal}}{\text{mole}}$

Then the reaction heat for each step in the oxy- $\beta$ -hydrogen abstraction pathway is found.

$$\Delta H_{E_1}^{\circ} = \Delta H_{f,(6)}^{\circ} - \Delta H_{f,(2)}^{\circ}$$

The O'Neal-Blumstein value of  $\Delta H_{f,(2)}^{\circ} = 0 \frac{\text{kcal}}{\text{mole}}$  ,

$$\Delta H_{E_1}^{\circ} = -9.0 - 0 = -9.0 \frac{\text{kcal}}{\text{mole}}$$

The approximation value of  $\Delta H_{f,(2)}^{\circ} = +14.2 \frac{\text{kcal}}{\text{mole}}$  ,

$$\Delta H_{E_1}^{\circ} = -9.0 - 14.2 = -23.2 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_{E_2}^{\circ} = \Delta H_{f,(7)}^{\circ} - \Delta H_{f,(8)}^{\circ} = -53.9 - (-9.0) = -44.9 \frac{\text{kcal}}{\text{mole}}$$

$$\begin{aligned} \Delta H_{E_3}^{\circ} &= \Delta H_{f,(8)}^{\circ} + \Delta H_{f,(9)}^{\circ} - \Delta H_{f,(7)}^{\circ} \\ &= -75.1 - 39.3 + 53.9 = -60.5 \frac{\text{kcal}}{\text{mole}} \end{aligned}$$

The thermochemistry of three other representative abstraction pathways (F, G, and O) was calculated as shown for the oxy- $\beta$ -abstraction case. The results of the calculations for 1-butene are summarized in Table 1.

### Summary

Various pathways of the O'Neal-Blumstein mechanism for gas phase ozonolysis have been compared thermochemically, using the  $O_3 + 1\text{-butene}$  reaction as a model. Working through this model reaction has resulted in several accomplishments:

- a) Additive  $\Delta H_f^{\circ}$  values for certain unlisted groups were calculated:



Group	$\Delta H_f^\circ$ , $\frac{\text{kcal}}{\text{mole}}$
•O-(O)	+21.3
•O-(C)	+13.6

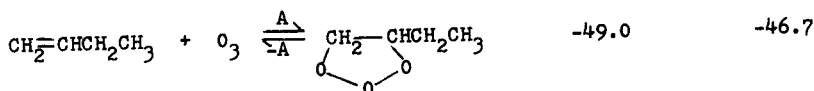
- b) A systematic method for evaluating the thermochemistry of individual compounds and pathways was developed. This method can easily be applied to other alkenes, since it is systematic and is based on tabulated materials.
- c) The heat of reaction for the Criegee split was found to be more exothermic than in O'Neal's and Blumstein's calculations because the heat of formation of species (2) (the biradical produced upon ring-opening in the molozonide) was lower than the O'Neal-Blumstein value. Since every pathway begins with the oxy-peroxy biradical as a reactant, each of the hydrogen abstraction reactions is more exothermic than in the O'Neal-Blumstein calculations. Therefore, the relative favorability of the cleavage and abstraction pathways is the same as predicted by the O'Neal-Blumstein calculations.

Table 1:

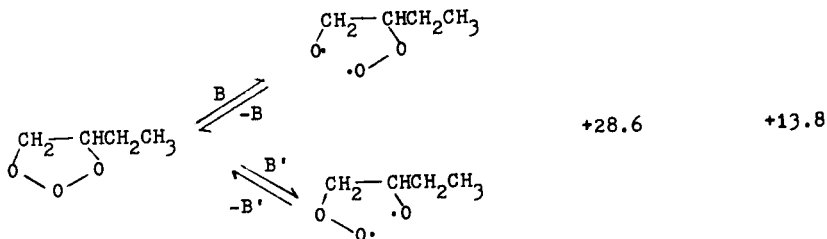
Thermochemistry for Selected Pathways  
of the O'Neal-Blumstein Ozonolysis Mechanism for 1-Butene

$\Delta H^\circ_{\text{calc, mole}}$   $\frac{\text{kcal}}{\text{mole}}$  <sup>27</sup>  $\Delta H^\circ_{\text{lit, mole}}$   $\frac{\text{kcal}}{\text{mole}}$  <sup>28</sup>

Molozonide Formation



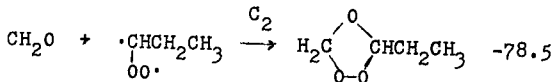
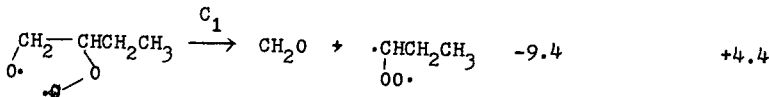
Biradical Formation



$$\Delta H_{\text{calc}}^{\circ} \frac{\text{kcal}}{\text{mole}}^{27} \quad \Delta H_{\text{lit}}^{\circ} \frac{\text{kcal}}{\text{mole}}^{28}$$

# REACTIONS OF THE BIRADICAL

## Criegee Split

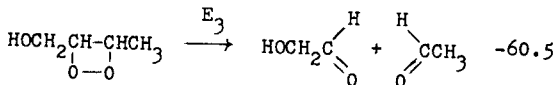
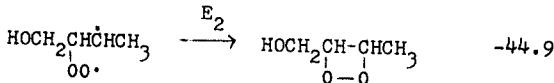
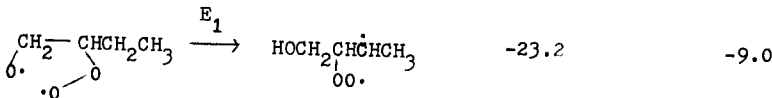


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$$\Delta H_{\text{C}}^{\circ} = -87.9^{27}$$

$$= -73.6^{28}$$

## Oxy-β-Hydrogen Abstraction



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$$\Delta H_{\text{E}}^{\circ} = -128.6^{27}$$

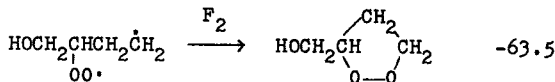
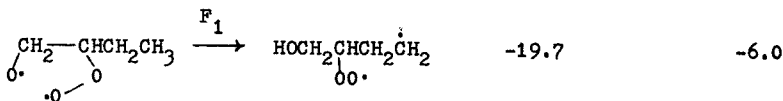
$$= -114.4^{28}$$

- 26 -

$\Delta H_{\text{calc}}^{\circ}$  kcal/mole <sup>27</sup>

$\Delta H_{\text{lit}}^{\circ}$  kcal/mole <sup>28</sup>

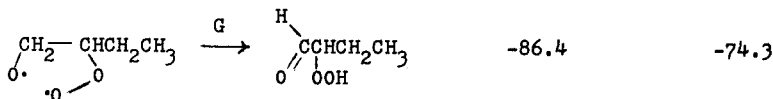
Oxy- $\gamma$ -Hydrogen Abstraction



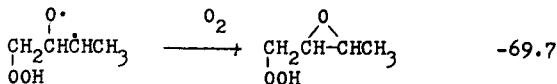
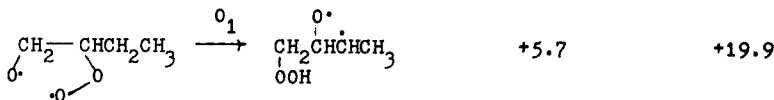
$$\Delta H_{\text{F}}^{\circ} = -83.2 \quad ^{27}$$

$$= -69.5 \quad ^{28}$$

Peroxy- $\alpha$ -Hydrogen Abstraction



Peroxy- $\beta$ -Hydrogen Abstraction



$$\Delta H_{\text{O}}^{\circ} = -64.0 \quad ^{27}$$

$$= -49.8 \quad ^{28}$$

### LITERATURE REVIEW

The work outlined in this section indicates progress toward the understanding of gas-phase ozonolysis of olefins from 1929 to the present. The 1950's showed a dramatic increase of interest in the gas-phase reaction, corresponding to the realization that ozone is a product of the photochemical decomposition of nitrogen dioxide in air.<sup>29,30</sup> Atmospheric ozonolysis reactions were found to produce plant toxicants, eye irritants, and smog.<sup>11,31-37</sup>

Interest in the chemistry of the atmosphere has continued to grow.<sup>38-44</sup> In addition to studies of gaseous smog components, efforts have been made to investigate particulate matter. Aerosol formation has been reported in several ozonolysis studies.<sup>10,11,33,35,45-47</sup> Some workers have attempted to identify the aerosol products<sup>48</sup> and their role in photochemical smog.<sup>38,49,50</sup> Current work includes attempts to determine the atmospheric fate of organic toxic substances by assessing individual effects of various chemical and physical removal processes.<sup>50-52</sup> Studies of the products and rates of the reaction of ozone with organic pollutants constitute an important facet of this work.

Considerable progress has been made in the accumulation of gas phase ozone-alkene product data, as summarized in Table 2. The period from 1929 to 1949 resulted in some introductory information about ozonolysis products, based to-

tally upon chemical analyses and analogy with solution-phase work. The development of increasingly sophisticated analytical methods has led to work at lower concentrations and more complete product studies. In the 1950's, product analyses utilized infrared spectroscopy.<sup>10,11,33,35,53,54</sup> The addition of ultraviolet spectroscopy and gas-liquid chromatographic analysis in the 1960's facilitated product identification and expanded the possibilities for quantitative work.<sup>45,46,48,55-58</sup> Experimental work of the 1970's depended upon gas chromatography, mass spectrometry, and gc/ms.<sup>14,15,34,59,60,62,63</sup> The application of mass spectrometric analysis proved to be a major breakthrough, as it is a more sensitive method for identification of stable products and also provides information about free-radical intermediates produced in ozonolysis reactions.<sup>64-66</sup> A recent ozonolysis study<sup>67</sup> couples gas-phase nmr with gc/ms to probe for less stable products such as peroxides, which may decompose as a result of gas chromatographic analysis.

Future work can be expected to include chemiluminescence spectroscopy. In ozone-olefin reactions conducted at low total pressures, fluorescence has been observed.<sup>15,16,68</sup> Chemiluminescence techniques have been applied successfully to the study of this phenomenon<sup>13,69-74</sup> and will probably become increasingly valuable for probing excited state and free-radical intermediates in ozonolysis reactions.<sup>12,59,60,75-77</sup>

This summary of studies of the gas-phase reaction of ozone with olefins concentrates on products; purely kinetic work is not included. Reactant concentrations span a wide range, but the majority of the work (86 out of 110 studies) has been done with initial concentrations of several thousand parts per million. The products for the lower molecular weight ( $\leq C_6$ ) 1-olefins are fairly well characterized.<sup>11,14,15,33-35,45,53,56-58,78,79</sup> Some work has been done on the straight-chain and branched olefins up to  $C_7$ , and recent studies include aromatic hydrocarbons<sup>62</sup> and terpenes.<sup>67</sup>

Table 2 lists the products observed for the gas-phase ozonolysis of each olefin. Yields are expressed in a variety of ways, as explained in the footnotes. Also included for each study are the initial concentrations of ozone and olefin, the total pressure of the reaction mixture, and the method of product analysis. Gases listed as diluents were added to the reaction mixture to obtain the desired total pressure. Some studies were not conducted at room temperature. The temperatures for these reactions are listed below the total pressure of the reactant mixture. Rate constants are listed for ozonolysis studies which included absolute or relative rate data.

Although recombination of the Criegee split fragments (carbonyl + zwitterion) to form the monomeric ozonide has been substantiated in low-temperature ( $-70^\circ C$ ) solution-

phase work,<sup>80,81</sup> the bimolecular recombination and dimerization reactions appear to be disfavored in the gas phase. In only a few cases is the formation of secondary ozonides reported. Propylene ozonide was found to be a major product in a single low-temperature gas phase study in an argon environment.<sup>46</sup> The formation of monomeric ozonides at room temperature has been reported (with yields of less than 20%) for cis-2-butene,<sup>63</sup> and also for 1-pentene, 1-hexene, and 3-heptene.<sup>35</sup> In addition, the 1-hexene reaction produced a small amount of "internal ozonide", a secondary ozonide with a  $C_4H_7$  chain on each end.<sup>35</sup>

The vast majority of gaseous ozonolysis work has resulted in the Criegee split carbonyl species as the major product. This supports the hypothesis that recombination to form the secondary ozonide is disfavored in the gas phase. Several sources indicated that a portion of the carbonyl products are initially "bound" as peroxide or peracid intermediates.<sup>11,33,34,53,56,78,79</sup> These species are "freed" as a result of the analysis procedure, producing aldehydes and ketones as stable products.

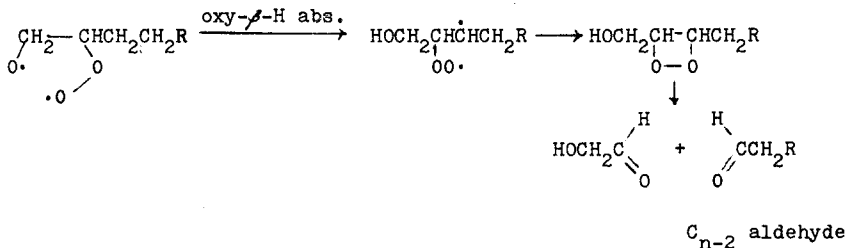
The products for the  $C_4$ ,  $C_5$ , and  $C_6$  1-olefins provide some insight into comparative advantages of the Criegee and O'Neal-Blumstein proposals in explaining the mechanism of gas-phase ozonolysis.<sup>11,34,45,56</sup> The major carbonyl product is an aldehyde containing one less carbon than the original olefin, resulting from addition of ozone across the



double bond and eventual cleavage. Another aldehyde, two carbons shorter than the original chain, is also produced. This carbonyl product, which is about one third as abundant as the major aldehyde, corresponds to cleavage of the C-C bond  $\alpha$  to the olefin  $\pi$ -bond. For example, consider 1-butene,<sup>56</sup>

major product: (0.48 relative to $O_3$ )	$CH_3CH_2CHO$	"normal" carbonyl product
lesser product: (0.133 relative to $O_3$ )	$CH_3CHO$	so-called "unusual" carbonyl product

The 3-carbon "normal" aldehyde is predicted by the Criegee split, which is also recognised as a possible pathway in the O'Neal-Blumstein mechanism. Criegee's mechanism offers no plausible explanation for the cleavage of the  $\alpha$ -carbon bond, whereas O'Neal and Blumstein predict the formation of  $C_{n-2}$  carbonyl products via cleavage of a 1,2-dioxetane intermediate:



$C_{n-2}$  aldehyde

This evidence lends support to the O'Neal-Blumstein mechanism for gas-phase ozonolysis.

Comparison of ozonolysis of the same olefin at low and high concentrations reveals large variations in the amount of carbon dioxide produced. For example, consider 1-pentene:

65 ppm 1-pentene,	
32 ppm ozone	yield: 9% CO <sub>2</sub> , relative to olefin <sup>33</sup>

3300 ppm 1-pentene,	
3300 ppm ozone	yield: 46% CO <sub>2</sub> , relative to olefin <sup>11</sup>

Although both the Criegee and O'Neal-Blumstein mechanisms suggest reactions which would generate CO<sub>2</sub>, one may question whether these ozonolysis pathways can account for the large amounts reported in high-concentration studies. Some ozonolysis reactions at high concentrations were accompanied by significant warming of the reaction vessel and in some cases even emission of light.<sup>46,48,56,60</sup> These are signs of combustion rather than ozonolysis of the olefin, and could account for the markedly greater yield of carbon dioxide at high concentrations. The possibility of olefin combustion in competition with the ozonolysis reaction could change significantly the resultant product mixtures and thus obscure any mechanistic information that may be obtained from such product studies. Therefore, there exists some question of the validity of high-concentration work in explaining the

mechanism of gas phase ozonolysis of olefins.

Although a significant amount of ozone-olefin product data has been gathered, the mechanism of gas phase ozonolysis is still not thoroughly understood. Several aspects of the reaction are worthy of additional research. Topics of interest include the formation of free-radical intermediates and excited-state products, the production of aerosols, and products of ozonolysis reactions involving more complex olefins. Comparison of high and low concentration work and efforts to assess the relative favorability of the various pathways suggested by O'Neal and Blumstein could also provide useful mechanistic information.

Specific details of the ozonolysis mechanism can be elucidated by noting how characteristics of the olefinic reagent affect the final product mixture. In this study, the ozonolysis of tetramethylethylene is investigated. The composition of the product mixture should provide insights into the relative favorability of various pathways in the O'Neal-Blumstein mechanism. Tetramethylethylene was chosen because it is symmetric about the double bond and has no hydrogens attached to the doubly bonded carbon atoms. The symmetry of the molecule simplifies mechanistic considerations somewhat because fission of either O-O bond in the primary ozonide results in the same biradical. Also, cleavage of the double bond creates only one carbonyl product, acetone.

The doubly bonded carbons cannot be involved in abstraction processes, as they bear no hydrogen atoms.

Several workers have reported cleavage of the C-C bond  $\alpha$  to the double bond in ozonolysis reactions.<sup>11,14,34,35, 45,48,54,56-59,63</sup> Some have tried to explain such cleavage products in terms of ozone-catalyzed allylic attack of molecular oxygen.<sup>45,48</sup> Ozonolysis of tetramethylethylene could be useful in probing possible  $\alpha$ -cleavage pathways, as it contains only  $\alpha$  C-C bonds in addition to the double bond.

The summary table of olefin ozonolysis cites five studies which involve tetramethylethylene. All five were completed more than a decade before the proposal of the O'Neal-Blumstein mechanism, and therefore include Criegee-type explanations of products. Schemes 3 and 4 show the Criegee and O'Neal-Blumstein mechanisms for the ozonolysis of tetramethylethylene. Some of the advantages of using the O'Neal-Blumstein proposal to rationalize gas phase ozonolysis are illustrated by comparison of the products predicted in each mechanism with actual results reported for tetramethylethylene.

In three of the studies, analysis of the product mixture was not the primary interest. Although these investigations list only one or two ozonolysis products, they provide some information which has value in the consideration of mechanistic possibilities.

Acetone was reported as a product of the  $O_3$ -tetramethylethylene reaction in a kinetic study by Vrbaski and Cvetanovic'.<sup>55</sup> Formation of acetone is rationalized in the Criegee mechanism by decomposition of the primary ozonide to yield a carbonyl product and a 3-carbon zwitterion fragment which may then react further. This possibility is included as the "Criegee split" pathway (C) in the O'Neal-Blumstein mechanism.

Tetramethylethylene was used by Hanst and Calvert to monitor the presence of ozone in a study of the mechanism of photo-oxidation of azomethane.<sup>54</sup> The reported products are assumed to be formed as a result of ozonolysis because azomethane- $O_3$  mixtures (with no tetramethylethylene present) were found to be unreactive. In addition to acetone, formaldehyde was formed, indicating that the C-C bond  $\alpha$  to the double bond was cleaved. The Criegee mechanism provides no reasonable rationale for cleavage of this sort. However, O'Neal and Blumstein explain the formation of formaldehyde as  $\beta$ -hydrogen abstraction by the oxy radical, followed by ring closure and subsequent cleavage (path G). Recombination of the Criegee split products does not appear to occur, as no ozonides were detected.

A comparative study of ozonolysis in the presence and absence of molecular oxygen by Wei and Cvetanovic',<sup>45</sup> provides some additional information about the reaction of tetramethylethylene with ozone. Acetone and carbon dioxide were produced, and an aerosol was formed. The ratio of olefin

consumed to ozone was found to be unity in a nitrogen environment. Since olefin consumption was greater than stoichiometric in the presence of molecular oxygen, secondary attack on the olefin was postulated. This explanation is understandable in terms of the O'Neal-Blumstein mechanism, since several pathways produce free radicals and highly reactive peroxides which may in turn attack any unreacted olefin present.

Two studies involve fairly complete product analyses for the ozonolysis of tetramethylethylene.<sup>48,56</sup> Both were at high concentrations ( $\geq 17,000$  ppm olefin) and reported significant warming upon mixing of the reactants, accompanied by the production of carbon dioxide. Various one-, two-, and three-carbon fragments were formed, corresponding to cleavage of both the single and double carbon bonds. In addition, Smith and Eastman<sup>48</sup> reported the formation of methyl acetate, which may be interpreted as a rearrangement product of the biradical produced in the Criegee split pathway (path D). Both gaseous and aerosol portions of the product mixture were analyzed, and were found to contain the same compounds in roughly equivalent mole ratios.

The yield of acetone (0.132 per mole of olefin) is far less than the Criegee mechanism predicts. Since the only reaction possibility of the molozonide in the Criegee scheme is cleavage into carbonyl and zwitterion fragments, 1:1 stoichiometry is expected in the production of acetone. The

experimental yield can be explained by the O'Neal-Blumstein predictions because only one of several possible pathways leads to the production of acetone.

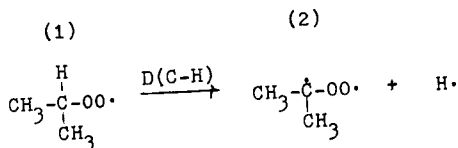
In this study, nearly twice as much olefin as ozone was consumed. This observation is not explainable in terms of the Criegee mechanism, which predicts 1:1 stoichiometry. The unexpectedly high consumption of olefin was rationalized by the proposal of two simultaneous reactions: attack of ozone at the double bond, and attack of molecular oxygen at the allylic position of the olefin.

The work of Vrbaski and Cvetanovic,<sup>56</sup> produced final product mixtures similar to those reported by Cvetanovic' and Wei.<sup>45</sup> Peroxidic intermediates ("bound" carbonyl products) were shown to be present by a positive KI test before GLC analysis. These products were assumed to be reduced to the corresponding carbonyl products as a result of the analysis procedure. The Criegee mechanism does not predict the formation of peroxidic intermediates, whereas several O'Neal-Blumstein pathways involve these highly reactive species.

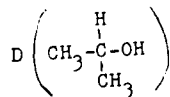
The O'Neal-Blumstein mechanism is the more complete description of gas phase ozonolysis because it contains several abstraction pathways in addition to all of the Criegee possibilities. The previous experimental observations illustrate that O'Neal's and Blumstein's proposal is more informative than the Criegee mechanism in explaining the ozonolysis

of tetramethylethylene. Consideration of thermochemical aspects of the various proposed pathways could provide insight into their relative favorability.

The thermochemistry of the reaction of tetramethylethylene with ozone was calculated as for the model 1-butene case. Radical group additivity values for  $\cdot O-(O)$  and  $\cdot O-(C)$  which were determined as part of the 1-butene reaction were used in these calculations. As before, the heat of formation of the radical species produced in the Criegee split was not directly available. Using the method of Wadt and Goddard,<sup>24</sup> the needed heat of formation value was estimated by considering the appropriate dissociation reaction:



$\Delta H_{f, (1)}^\circ$  and  $\Delta H_f^\circ (\text{H}\cdot)$  are available, and the C-H bond dissociation energy was found by considering



and correcting for the additional stabilization of the C-O  $\pi$ -bond. Then  $\Delta H_{f, (2)}^\circ$  could be calculated.


The thermochemistry of each step and each pathway is included in the O'Neal-Blumstein mechanism for tetramethyl-




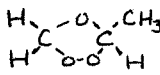

ethylene (Scheme 4). The overall heat of reaction for each pathway is negative, indicating that all pathways are exothermic and therefore thermochemically allowed. Certain steps ( $C_1$ ,  $F_1$ , and  $H_1$ ) involve positive heats of reaction which may affect the relative favorability of the pathways to which they lead. One may note that the two paths which are predicted to be the most exothermic (D and G) result in the formation of compounds which have already been reported as products of the ozonolysis of tetramethylethylene, namely, methyl acetate and formaldehyde.

Previous work involving the gas phase ozonolysis of tetramethylethylene which is discussed in this section indicates several aspects of the reaction which merit further investigation. In this work a study was made of the products of the tetramethylethylene-ozone reaction at low initial concentrations ( $\leq 800$  ppm). Comparison of relative product yields and the stoichiometry of reaction for low and high concentration work is valuable to understanding the mechanism of ozonolysis. Trends observed in the product mixture over a range of initial reactant concentrations should also provide mechanistic information.

TABLE 2:  
PREVIOUS WORK IN THE GAS PHASE OZONOLYSIS OF VARIOUS OLEFINS

OLEFIN	[OLEFIN] (PPM)	[OZONE] (PPM)	TOTAL PRESSURE (mmHg)	DILUENT GAS	ANALYSIS METHOD	$K$ $\left(\frac{L}{mol \cdot sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> <sup>84</sup>	≤ 2	~ 1	760	AIR	GLC	$2.0 \times 10^3$	ABSOLUTE	HCHO	0.7	57
C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> <sup>84</sup>	32	32	760	O <sub>2</sub>	IR	—	—	H <sub>2</sub> O CO H <sub>2</sub> CO CO <sub>2</sub> HCOOH	0.9 0.9 0.5 0.13 < 0.03	33
C <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	395	~ 53	2	O <sub>2</sub>	MS	—	—	HCHO	MAJOR	14
C <sub>2</sub> C <sub>2</sub> H <sub>4</sub> <sup>83</sup>	26,000- 52,000	3000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	HCOOH CH <sub>3</sub> CHO	0.25 0.019	56
C <sub>2</sub> C <sub>2</sub> F <sub>4</sub>	260- 7,500	960- 32,000	1-24 t = -60°C	—	IR	$8.1 \times 10^4$	ABSOLUTE	CF <sub>2</sub> O CF <sub>3</sub> CFO O <sub>2</sub>	— — —	58
C <sub>3</sub>  <sup>84</sup>	32	32	760	O <sub>2</sub>	IR	—	—	H <sub>2</sub> O CO H <sub>2</sub> CO CH <sub>3</sub> CHO CO <sub>2</sub> H <sub>2</sub> C=C=O Acids	1.6 0.63 0.5 0.38 0.28 0.3-0.6 < 0.6	33










OLEFIN #	[OLEFIN] (ppm)	[Ozone] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K $\left(\frac{L}{\text{mole-sec}}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>3</sub> <sup>83</sup>	12,000-75,000	25,000	760 t=48-78°C	AIR	CHEMICAL ANALYSIS	-	-	HCHO CH <sub>3</sub> CHO HCOOH CH <sub>3</sub> COOH	- - - -	78
C <sub>3</sub> <sup>83</sup>	26,000-52,000	3,000-13,000	100-440	O <sub>2</sub>	GLC	-	-	CH <sub>3</sub> CHO HCOOH CO <sub>2</sub> CH <sub>3</sub> OH CH <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> OCHO C <sub>2</sub> H <sub>5</sub> CHO	0.38 0.34 0.32 0.033 0.008 0.003 0.003	56
C <sub>3</sub> <sup>85</sup>	52,000	3,250	110-135	O <sub>2</sub>	GLC	1.41	<sup>85</sup>	CH <sub>3</sub> CHO	0.551 RELATIVE TO <sup>85</sup>	55
C <sub>3</sub> <sup>83</sup>	29,000	4,900	100	O <sub>2</sub>	GLC	1.30	<sup>83</sup>	CH <sub>3</sub> CHO	0.34	45
C <sub>3</sub> <sup>83</sup>	29,000	4,900	100	N <sub>2</sub>	GLC	0.95	<sup>83</sup>	CH <sub>3</sub> CHO	0.27	45
C <sub>3</sub> <sup>83</sup>	2.6-8.4	1.2	<0.1	-	MS	8.73 x 10 <sup>3</sup>	ABSOLUTE	CH <sub>3</sub> CHO CO <sub>2</sub> CO HCOOH HCHO H <sub>2</sub> C=C=O	MAJOR   MINOR MINOR MINOR	15

OLEFIN 42	[OLEFIN] (ppm)	[OLÉNE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K ( $\frac{L}{mole-sec}$ )	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>3</sub> 	40,000- 180,000	8,500- 18,000	760 t = -90- -40°C	Ar	IR	—	—		MAJOR	46
C <sub>3</sub> <sup>84</sup> CH <sub>2</sub> =C=CH <sub>2</sub>	3,600	~90	~3	—	GC	—	—	CO H <sub>2</sub> O O <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	0.08 0.04 0.032 0.019 0.0045	60
C <sub>3</sub> <sup>84</sup> CH <sub>2</sub> =C=CH <sub>2</sub>	3,400	220	~55	O <sub>2</sub>	GC	—	—	CO O <sub>2</sub> H <sub>2</sub> O C <sub>2</sub> H <sub>4</sub>	0.046 0.027 0.014 0.033	60
C <sub>3</sub> <sup>84</sup> CH <sub>2</sub> =C=CH <sub>2</sub>	6,700	350	~44	CO <sub>2</sub>	GC	—	—	CO <sub>2</sub> H <sub>2</sub> O C <sub>2</sub> H <sub>4</sub>	0.018 0.011 0.0031	60
C <sub>3</sub> C <sub>3</sub> F <sub>6</sub>	240- 9,200	2,500- 19,000	2.5- 15 t = 60°C	—	IR	1.3 × 10 <sup>4</sup>	ABSOLUTE	CF <sub>2</sub> O CF <sub>3</sub> CFO O <sub>2</sub>	— — —	58
C <sub>4</sub> 	≤ 2	~1	760	AIR	GLC	8.5 × 10 <sup>3</sup>	ABSOLUTE	CH <sub>3</sub> CH <sub>3</sub>	MINOR.	57

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


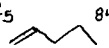
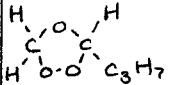
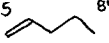

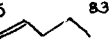
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










OLEFIN 45	[OLEFIN] (PPM)	[OZONE] (PPM)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K $\left(\frac{\text{L}}{\text{mole-sec}}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
$\text{C}_4 \text{ } \text{CH}_3\text{CH=CHCH}_3$	29,000	4,900	100	$\text{N}_2$	GLC	—	—	$\text{CH}_3\text{COCH}_3$ $\text{CO}_2$ $\text{CH}_3\text{CHO}$	0.33 0.15 0.006	45
$\text{C}_4 \text{ } \text{CH}_3\text{CH=CHCH}_3$	10	5	700	AIR	LONG-PATH FT-IR	—	—	$\text{H}-\text{C}(\text{O})-\text{O}-\text{C}(\text{O})-\text{H}$ $\text{H}_3\text{C}-\text{O}-\text{C}(\text{O})-\text{CH}_3$ $\text{CH}_4$ $\text{HCHO}$ $\text{HCOOH}$ $\text{CH}_3\text{OH}$ $\text{CH}_3\text{CHO}$ $\text{CH}_2\text{CO}$ $\text{CO}$ $\text{CO}_2$	0.18	63
$\text{C}_4 \text{ } \text{CH}_3\text{CH=CHCH}_3$	395	~53	2	$\text{O}_2$	MS	—	—	$\text{HCHO}$ $\text{CH}_3\text{CHO}$ $\text{CH}_2\text{CO}$ $\text{H}-\text{C}(\text{O})-\text{C}(\text{O})-\text{H}$ $\text{HCOOH}$ $\text{CH}_3\text{OH}$ $\text{H}_2\text{O}_2$	MAJOR MAJOR MAJOR MINOR MINOR MINOR MINOR	14











OLEFIN 46	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K ( $\frac{L}{mole-sec}$ )	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>4</sub>  <sup>83</sup>	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	CH <sub>3</sub> CHO CO <sub>2</sub> HCOOH CH <sub>3</sub> OH C <sub>3</sub> H <sub>6</sub> C <sub>4</sub> H <sub>10</sub>	1.02 0.42 0.20 0.152 0.023 TRACE	56
C <sub>4</sub>  <sup>85</sup>	26,000	1,300	50-60	O <sub>2</sub>	GLC	3.69		CH <sub>3</sub> CHO	1.53 RELATIVE TO 	55
C <sub>4</sub>  <sup>83</sup>	29,000	4,900	100	O <sub>2</sub>	GLC	3.4		CH <sub>3</sub> CHO CO <sub>2</sub>	0.98 0.35	45
C <sub>4</sub>  <sup>83</sup>	29,000	4,900	100	N <sub>2</sub>	GLC	2.0		CH <sub>3</sub> CHO CO <sub>2</sub>	0.68 0.19	45
C <sub>4</sub> 	~400	~50	2-10	O <sub>2</sub>	GC, MS	6.3x10 <sup>4</sup>	ABSOLUTE	CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub> COCH=CH <sub>2</sub> CH <sub>2</sub> =C=O CH <sub>3</sub> OH CH <sub>3</sub> CHCOCH <sub>3</sub> SOH HCHO	MAJOR MAJOR MAJOR MAJOR	59
C <sub>4</sub> C <sub>4</sub> H <sub>8</sub> <sup>87</sup>	40,000- 50,000	80,000	760 t=40- 70°C	O <sub>2</sub>	CHEMICAL ANALYSIS	—	—	CH <sub>3</sub> COCH <sub>3</sub> ALDEHYDES ACIDS	— — —	79














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






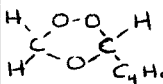
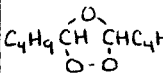
OLEFIN 48	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k $\left(\frac{L}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>4</sub>  <sup>85</sup>	52,000	3,250	110-135	O <sub>2</sub>	GLC	1.07		CH <sub>2</sub> =CHCHO	0.726 RELATIVE TO 	55
C <sub>4</sub> C <sub>4</sub> F <sub>8</sub> <sup>87</sup>	250-8,800	1700-110,000	4-85 t=60°C	—	IR	1.1 × 10 <sup>3</sup>	ABSOLUTE	CF <sub>2</sub> O CF <sub>3</sub> CFO O <sub>2</sub>	— — —	58
C <sub>5</sub>  <sup>84</sup>	20	20	760	AIR	LONG-PATH IR	4.5 × 10 <sup>3</sup>	ABSOLUTE	 H <sub>2</sub> O C <sub>3</sub> H <sub>7</sub>	0.08	35
C <sub>5</sub>  <sup>84</sup>	65	32	760	O <sub>2</sub>	IR	—	—	H <sub>2</sub> O n-C <sub>3</sub> H <sub>7</sub> CHO CO H <sub>2</sub> CO CO <sub>2</sub> ACIDS	0.77 0.25 0.23 0.22 0.09 <0.02	33
C <sub>5</sub>  <sup>84</sup>	3,300	3,300	760	AIR	IR	—	—	CO CO <sub>2</sub> n-C <sub>3</sub> H <sub>7</sub> CHO HCOOH OTHER CARBOXYL COMPOUNDS	0.66 0.46 ~0.4 — ~0.1	11
C <sub>5</sub>  <sup>83</sup>	~400-10,000	~400-10,000	760	AIR	IR	—	—	n-C <sub>4</sub> H <sub>9</sub> CHO CO <sub>2</sub> HCOOH	~0.7 ~0.2 —	53

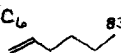
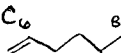
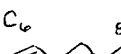

OLEFIN 49	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K ( $\frac{L}{mole-sec}$ )	RELATIVE TO	PRODUCTS	Y. YLD	REF.
C <sub>5</sub>  83	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	-	-	n-C <sub>5</sub> H <sub>7</sub> CHO CO <sub>2</sub> HCOOH C <sub>2</sub> H <sub>5</sub> CHO C <sub>3</sub> H <sub>8</sub> CH <sub>3</sub> CHO C <sub>3</sub> H <sub>6</sub>	0.32 0.29 0.20 0.161 0.129 0.061 0.046	56
C <sub>5</sub>  85	52,000	3,250	110- 135	O <sub>2</sub>	GLC	0.236		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	0.515 RELATIVE TO 	55
C <sub>5</sub>  83	29,000	4,900	100	O <sub>2</sub>	GLC	1.10		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> CHO	0.32 0.24 0.087 0.019	45
C <sub>5</sub>  83	29,000	4,900	100	N <sub>2</sub>	GLC	0.85		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> CHO	0.24 0.16 0.053 0.053	45
C <sub>5</sub>  83	29,000	4,900	100	O <sub>2</sub>	GLC	3.4		CH <sub>3</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO CO <sub>2</sub>	0.52 0.45 0.36	45
C <sub>5</sub>  83	29,000	4,900	100	N <sub>2</sub>	GLC	2.4		CH <sub>3</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO CO <sub>2</sub>	0.32 0.30 0.20	45

OLEFIN 50	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K $\left(\frac{\text{L}}{\text{mole} \cdot \text{sec}}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>5</sub>  83	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	C <sub>2</sub> H <sub>5</sub> CHO CH <sub>3</sub> CHO CO <sub>2</sub> HCOOH C <sub>2</sub> H <sub>6</sub> CH <sub>3</sub> OH CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> n-C <sub>3</sub> H <sub>7</sub> CHO	0.56 0.56 0.30 0.20 0.014 0.013 0.001 0.0003	56
C <sub>5</sub>  85	52,000	3,200	110- 135	O <sub>2</sub>	GLC	2.84		CH <sub>3</sub> CH <sub>2</sub> CHO	0.763 RELATIVE TO 	55
C <sub>5</sub>  83	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	C <sub>2</sub> H <sub>5</sub> CHO CH <sub>3</sub> CHO CO <sub>2</sub> HCOOH C <sub>2</sub> H <sub>6</sub> C <sub>2</sub> H <sub>4</sub> CH <sub>3</sub> OH	0.56 0.56 0.36 0.16 0.096 0.018 0.012	56
C <sub>5</sub>  85	52,000	3,250	110- 135	O <sub>2</sub>	GLC	3.50		CH <sub>3</sub> CH <sub>2</sub> CHO	0.756 RELATIVE TO 	55
C <sub>5</sub>  83	29,000	4,900	100	O <sub>2</sub>	GLC	4.1		CH <sub>3</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO CO <sub>2</sub>	0.52 0.45 0.24	45

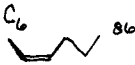
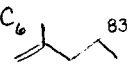
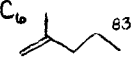
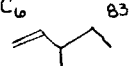
OLEFIN 51	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k $\left(\frac{l}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>5</sub>  83	29,000	4,900	100	N <sub>2</sub>	GLC	2.7		CH <sub>3</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO CO <sub>2</sub>	0.33 0.31 0.14	45
C <sub>5</sub>  84	≤ 2	~ 1	760	AIR	GLC	-	-	CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	> 0.2 0.2	57
C <sub>5</sub>  83	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	-	-	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> HCOOH CH <sub>3</sub> OH C <sub>4</sub> H <sub>8</sub> CH <sub>3</sub> CHO C <sub>3</sub> H <sub>6</sub> C <sub>3</sub> H <sub>8</sub>	0.43 0.29 0.24 0.058 0.026 - TRACE TRACE	56
C <sub>5</sub>  85	52,000	3,250	110- 135	O <sub>2</sub>	GLC	3.02		CH <sub>3</sub> CHO	1.35 RELATIVE TO 	55
C <sub>5</sub>  83	29,000	4,900	100	O <sub>2</sub>	GLC	3.5		CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub>	0.76 0.56 0.41	45
C <sub>5</sub>  83	29,000	4,900	100	N <sub>2</sub>	GLC	3.2		CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub>	0.40 0.33 0.15	45

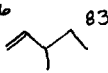

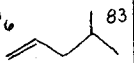

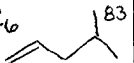

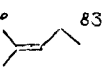

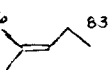

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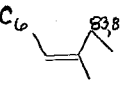

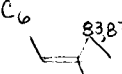

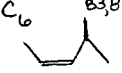

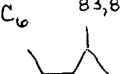

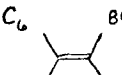
OLEFIN S	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k ( $\frac{l}{mole-sec}$ )	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>5</sub> 	29,000	4,900	100	N <sub>2</sub>	GLC	0.75		(CH <sub>3</sub> ) <sub>2</sub> CHCHO CO <sub>2</sub> CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	0.25 0.18 0.125 0.040	45
C <sub>5</sub> 	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	-	-	(CH <sub>3</sub> ) <sub>2</sub> CHCHO CO <sub>2</sub> HCOOH C <sub>3</sub> H <sub>8</sub> C <sub>3</sub> H <sub>6</sub> CH <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> CHO CH <sub>3</sub> OH CH <sub>3</sub> OCHO	0.30 0.29 0.25 0.132 0.081 0.074 0.032 0.015 0.001	56
C <sub>5</sub> 	52,000	3,250	110- 135	O <sub>2</sub>	GLC	0.79		(CH <sub>3</sub> ) <sub>2</sub> CHCHO	0.985 RELATIVE TO 	55
C <sub>6</sub> 	≤ 2	~1	760	AIR	GLC	7.5 × 10 <sup>3</sup>	ABSOLUTE	C <sub>4</sub> H <sub>9</sub> CHO C <sub>4</sub> H <sub>10</sub>	MAJOR MINOR	57
C <sub>6</sub> 	11	11	760	AIR	LONG-PATH IR	6.1 × 10 <sup>3</sup>	ABSOLUTE	 	0.11 0.02	55











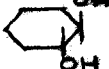
OLEFIN 54	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k $\left(\frac{L}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
	26,000- 52,000	3000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	HCOOH CO <sub>2</sub> n-C <sub>4</sub> H <sub>9</sub> CHO C <sub>4</sub> H <sub>10</sub> n-C <sub>3</sub> H <sub>7</sub> CHO C <sub>4</sub> H <sub>8</sub> CH <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> CHO C <sub>2</sub> H <sub>6</sub> C <sub>3</sub> H <sub>6</sub>	0.24 0.23 0.118 0.076 0.056 0.027 0.015 0.005 0.005 TRACE	56
	29,000	4,900	100	O <sub>2</sub>	GLC	1.25	Y=	n-C <sub>4</sub> H <sub>9</sub> CHO CO <sub>2</sub> n-C <sub>3</sub> H <sub>7</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> CHO	0.30 0.20 0.055 0.015 0.010	45
	29,000	4,900	100	N <sub>2</sub>	GLC	1.05	Y=	n-C <sub>4</sub> H <sub>9</sub> CHO CO <sub>2</sub> n-C <sub>3</sub> H <sub>7</sub> CHO CH <sub>3</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO	0.25 0.14 0.035 0.035 0.015	45
	29,000	4,900	100	O <sub>2</sub>	GLC	3.6	Y=	CH <sub>3</sub> CHO n-C <sub>3</sub> H <sub>7</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO	0.46 0.34 0.32 0.052	45


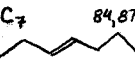
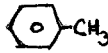
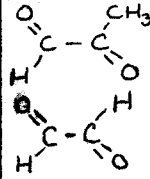


OLEFIN	[OLEFIN] (PPM)	[OZONE] (PPM)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k $\left(\frac{L}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
55 	29,000	4,900	100	N <sub>2</sub>	GLC	2.7	$\gamma$	CH <sub>3</sub> CHO n-C <sub>3</sub> H <sub>7</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO	0.32 0.25 0.18 0.040	45
	29,000	4,900	100	O <sub>2</sub>	GLC	1.30	$\gamma$	CH <sub>3</sub> COC <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	0.36 0.32 0.150 0.045 0.015	45
	29,000	4,900	100	N <sub>2</sub>	GLC	1.25	$\gamma$	CH <sub>3</sub> COC <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	0.22 0.14 0.075 0.035 0.035	45
	29,000	4,900	100	O <sub>2</sub>	GLC	0.90	$\gamma$	(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> )CHCHO CO <sub>2</sub> CH <sub>3</sub> CHO CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	0.30 0.26 0.050 0.050 0.003 0.002	45


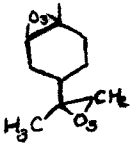
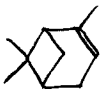
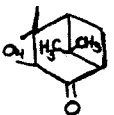
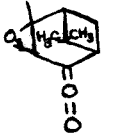
56 OLEFIN	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k $\left(\frac{\text{L}}{\text{mole-sec}}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>6</sub> 	29,000	4,900	100	N <sub>2</sub>	GLC	0.75		(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> )CHCHO CO <sub>2</sub> CH <sub>3</sub> CHO CH <sub>3</sub> COCH <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> COCH <sub>3</sub>	0.23 0.16 0.115 0.035 0.016 0.004	45
C <sub>6</sub> 	29,000	4,900	100	O <sub>2</sub>	GLC	1.15		(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHO CO <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CHCHO CH <sub>3</sub> COCH <sub>3</sub> CH <sub>3</sub> CHO	0.30 0.24 0.080 0.020 0.010	45
C <sub>6</sub> 	29,000	4,900	100	N <sub>2</sub>	GLC	0.85		(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CHO (CH <sub>3</sub> ) <sub>2</sub> CHCHO CH <sub>3</sub> COCH <sub>3</sub>	0.23 0.15 0.060 0.030 0.020	45
C <sub>6</sub> 	29,000	4,900	100	O <sub>2</sub>	GLC	3.5		CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> CHO	0.63 0.48 0.40 0.076	45
C <sub>6</sub> 	29,000	4,900	100	N <sub>2</sub>	GLC	3.2		CH <sub>3</sub> CH <sub>2</sub> CHO CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> CHO	0.36 0.26 0.13 0.036	45

57	OLEFIN (ppm)	[Oxone] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k ( $\frac{l}{mole-sec}$ )	RELATIVE TO	PRODUCTS	YIELD	REF.
	29,000	4,900	100	O <sub>2</sub>	GLC	3.4		CH <sub>3</sub> CHO CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub> COCH <sub>3</sub>	0.73 0.50 0.32 0.005	45
	29,000	4,900	100	N <sub>2</sub>	GLC	3.2		CH <sub>3</sub> CHO CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub> COCH <sub>3</sub>	0.39 0.30 0.11 0.001	45
	29,000	4,900	100	O <sub>2</sub>	GLC	3.5		(CH <sub>3</sub> ) <sub>2</sub> CHCHO CH <sub>3</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO	0.48 0.40 0.30 0.002	45
	29,000	4,900	100	N <sub>2</sub>	GLC	2.3		(CH <sub>3</sub> ) <sub>2</sub> CHCHO CH <sub>3</sub> CHO CO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CHO	0.33 0.30 0.18 0.010	45
	17,000	8,000	760	N <sub>2</sub> +O <sub>2</sub>	CHEMICAL ANALYSIS	—	—	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> COOH H <sub>2</sub> CO HCOOH CH <sub>3</sub> OH CH <sub>3</sub> OCOCH <sub>3</sub>	0.132 0.057 0.054 0.030 0.024 — —	48

OLEFIN	[OLEFIN] (PPM)	[KETONE] (PPM)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	R $\left(\frac{l}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	RELATIVE TO	YIELD
C <sub>6</sub>  84	17,800	~0.01	760	O <sub>2</sub>	IR	—	—	H <sub>2</sub> CO CH <sub>3</sub> COCH <sub>3</sub>	1.1 1.0	54
C <sub>6</sub>  83	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> HCOOH CH <sub>3</sub> CHO CH <sub>3</sub> OCHO CH <sub>3</sub> OH C <sub>2</sub> H <sub>6</sub>	1.49 0.40 0.22 0.010 0.007 — TRACE	50
C <sub>6</sub>  85	52,000	3,250	110- 135	O <sub>2</sub>	GLC	4.50		CH <sub>3</sub> COCH <sub>3</sub>	4.06 RELATIVE TO 	55
C <sub>6</sub>  82	29,000	4,900	100	O <sub>2</sub>	GLC	4.8		CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub>	1.45 0.42	45
C <sub>6</sub>  83	29,000	4,900	100	N <sub>2</sub>	GLC	5.5		CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub>	0.65 0.11	45
C <sub>6</sub>  84	19,500	12,000	760	N <sub>2</sub> +O <sub>2</sub>	UV, IR, CHEMICAL ANALYSIS	—	—	CO <sub>2</sub> H (CH <sub>2</sub> ) <sub>4</sub>   CO <sub>2</sub> H (ADIPIC ACID) HCOOH 	<0.5  0.1	10

OLEFIN No	[OLEFIN] (ppm)	[Olefin] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	$\frac{1}{\text{mg (at 5 cc)}}$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>6</sub> 	26,000- 52,000	3,000- 13,000	100- 440	O <sub>2</sub>	GLC	—	—	CO <sub>2</sub> HCOOH C <sub>2</sub> H <sub>4</sub> CH <sub>3</sub> CHO	0.59 0.29 0.118 0.014	56
C <sub>7</sub> 	//	//	760	AIR	Long Path IR	<del>5.2 x 10<sup>-4</sup></del>	ABSOLUTE	C <sub>2</sub> H <sub>5</sub> CH O-O-CH <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> =C=O H <sub>2</sub> O CH <sub>3</sub> OH CH <sub>4</sub> CO CO <sub>2</sub>	0.19 — — — — — —	35
C <sub>7</sub> 	~90	~80	760	AIR	GC, LONG-PATH IR, GC/MS	9.0 x 10 <sup>-2</sup>	ABSOLUTE	 CHO CO CO <sub>2</sub> HCOOH H <sub>3</sub> CCOOH	— — — — —	62

OLEFIN S	[OLEFIN] (PPM)	[OZONE] (PPM)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K $\left(\frac{L}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>8</sub> 	~90	~80	760	AIR	GC, LONG-PATH IR, GC/MS	0.42	ABSOLUTE	 CO CO <sub>2</sub> HCOOH CH <sub>3</sub> COOH 	— — — — —	62
C <sub>9</sub> 	~90	~80	760	AIR	GC, LONG-PATH IR, GC/MS	1.3	ABSOLUTE	 CO CO <sub>2</sub> HCOOH CH <sub>3</sub> COOH	— — — —	

OLEFIN 61	[OLEFIN] (ppm)	[OZONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	k $\left(\frac{L}{mole-sec}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
$C_{10}$  (DIPENTENE)		EXCESS	760	$O_2$	CHEMICAL ANALYSIS, COMBUSTION	—	—	 (DIPENTENE DIOZONIDE)	—	82
$C_{10}$  ( $\alpha$ -PINENE)		EXCESS	760	$O_2$	CHEMICAL ANALYSIS, COMBUSTION	—	—	 (VERBENONE OXO DIONIDE)  OR  (VERBENONE PEROXIDE OZONIDE)	—	

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RUSIK, C.A.

CHEMISTRY

THE GAS PHASE OZONOLYSIS OF, ETC.

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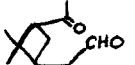
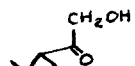
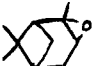
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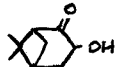

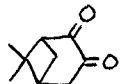
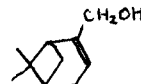
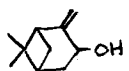
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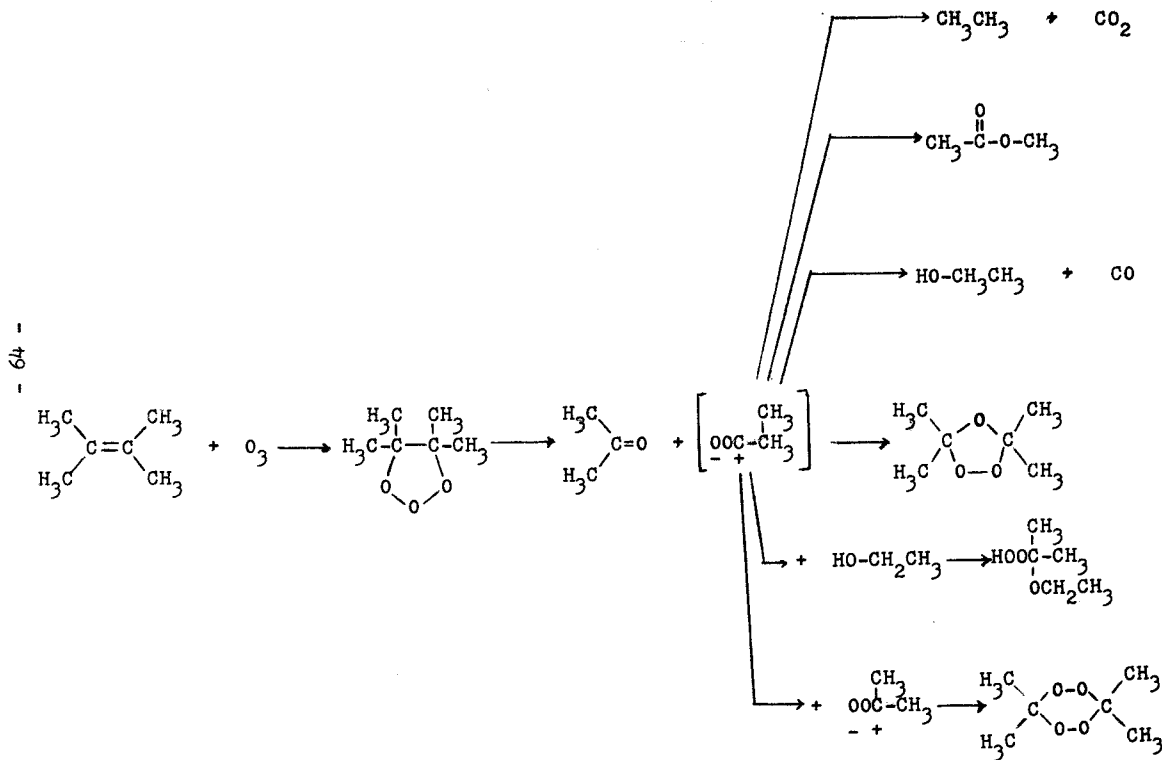
END



OLEFIN	[OLEFIN] (ppm)	[KETONE] (ppm)	TOTAL PRESSURE (mm Hg)	DILUENT GAS	ANALYSIS METHOD	K $\left(\frac{\text{L}}{\text{MOLE} \cdot \text{SEC}}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>10</sub>  ( $\alpha$ -PINENE)	16-500 ALWAYS IN EXCESS	4-300	760	AIR	GC/MS, NMR	—	—	 (CIS-PINONIC ACID)	27%	67
								 (PINONALDEHYDE)	15%	
								 (HYDROXY-PINONALDEHYDE)	7%	
								 ( $\alpha$ -PINENE EPOXIDE)	(TRACE)	

OLEFIN S	[OLEFIN] (PPM)	[OZONE] (PPM)	TOTAL PRESSURE (MM HG)	DILUENT GAS	ANALYSIS METHOD	K $\left(\frac{L}{MOLE-SEC}\right)$	RELATIVE TO	PRODUCTS	YIELD	REF.
C <sub>10</sub>	16-500 ALWAYS IN EXCESS	4-300	760	AIR	GC/MS, NMR	—	—	 (3-HYDROXY- NOPINONE)	28%	67
								 (NOPINONE)	10%	
								 (3-KETO- NOPINONE)	7%	
								 (MYRTENOL)	—	
								 (PINOCARVEOL)	—	

Scheme 3:  
Criegee Ozonolysis Mechanism for Tetramethylethylene



**Scheme 4:**

**O'Neal-Blumstein Ozonolysis Mechanism for Tetramethylethylene**

Δ H  
Pathway

-118.9

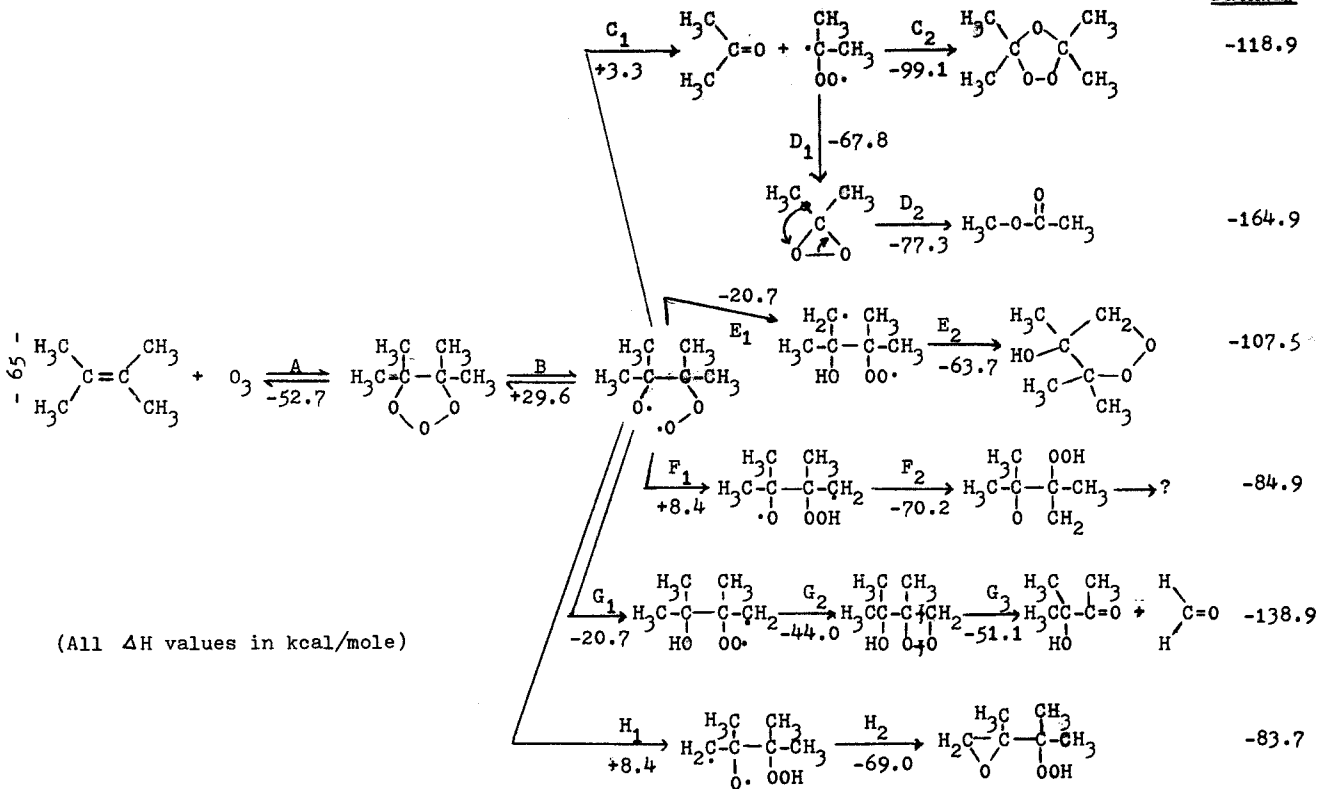
-164.9

-107.5

-84.9

-138.9

-83.7

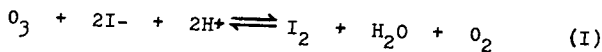


### EXPERIMENTAL

#### a) Ozone Analysis

The stoichiometry of the reaction of tetramethylethylene with ozone is important in terms of the mechanism of ozonolysis. A method of analysis for ozone was required, in order to know how much of this reactant was present.

The concentration of ozone in the reactant sample was determined by the oxidation of iodide ion to iodine in aqueous solution, which occurs according to the reaction:



This reaction is pH-dependent. Analysis of ozone requires either acid or neutral conditions, as the liberation of  $I_2$  by oxygen is favored in basic medium. The actual stoichiometry varies according to pH, so the aqueous KI solution is usually buffered. The traditional iodometric analysis procedure employs a phosphate buffer ( $KH_2PO_4/Na_2HPO_4$ ),<sup>88</sup> and has been found to produce hydrogen peroxide as a by-product. The  $H_2O_2$  produced reacts with  $I^-$  to liberate  $I_2$  15%-30% in excess of the stoichiometric equation.<sup>89</sup> In addition, phosphate buffer results appear to be affected by the humidity of the gas sample, and the degree of non-stoichiometry is a factor of the time period between absorption and analysis.<sup>90,91</sup>

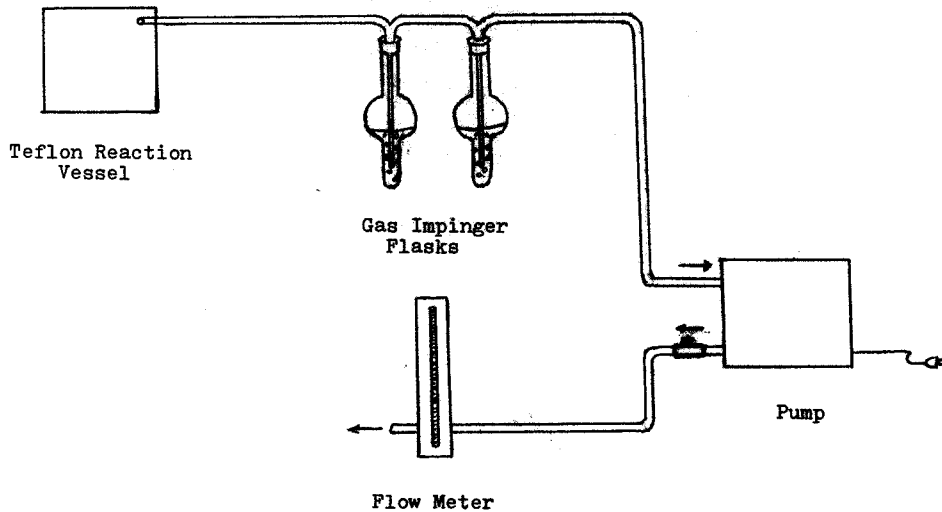
In this study, ozone concentrations were monitored by a method proposed by D. Flamm,<sup>89</sup> which employs an aqueous solution of 1% potassium iodide buffered with 0.1 M boric acid. This method was tested against ultraviolet photometric absorption in the 0.35-3.5 ppm range and was found to produce iodine quantitatively according to equation (I).<sup>89</sup>

The apparatus is shown in Figure 1. A known volume of boric acid buffered KI solution was placed in each gas impinger flask. A portion of the ozone sample was drawn through the impingers by a vacuum pump. The sampling flow rate was regulated by a valve on the pump outlet and was read off in liters/minute on the calibrated flow meter. Sample size is a function of flow rate and sampling time.

Flamm's analysis method was proposed for the concentration range 0.1-1 ppm. Since this study involves  $O_3$  concentrations ranging from 10 to 800 ppm, some adjustments in the analysis procedure were necessary. The proposed method was adapted to higher concentrations by decreasing the sample size and increasing the amount of KI solution in each impinger.

The amount of iodine liberated was determined from the absorbance of  $I_3^-$  at 352 nm, measured against a reference of fresh KI solution on a Cary 118 UV-Visible Spectrometer. The settings on the instrument were as follows:

Figure 1:  
Ozone Analysis Apparatus



Source: visible, normal intensity

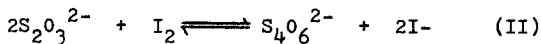
Mode : autoslit

Gain : 0.30

Period: 5 seconds

To ensure stable and accurate operation, the Cary-118 was allowed to warm up for at least one hour with fresh buffered KI solution in both the sample and reference cells. During analysis, the fresh KI solution used as the reference was replaced frequently and care was taken to limit the amount of time that the sample was exposed to the light beam. These precautions were taken in order to minimize error caused by the liberation of additional iodine, which is catalyzed by the analyzing beam.

Solutions of iodine in the buffered KI solution were prepared and standardized by titration with thiosulfate:

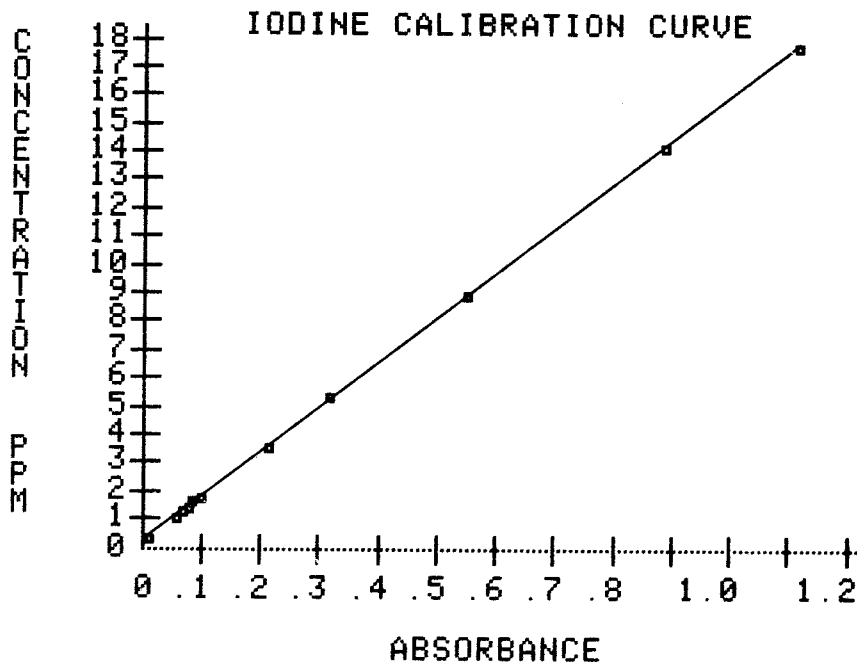


Absorbance values for the standardized  $I_2$  solutions provided a calibration curve for the ozone determination (Figure 2).

Buffered KI solutions were stored in a dark cabinet to minimize photolytic liberation of  $I_2$ . An air blank was used to test for the presence of extraneous oxidizing agents which would liberate additional iodine. The absorbance of the air blank was within experimental error of the absorbance value



Figure 2:  
Calibration Curve--Iodine in Buffered KI Solution



$$m = 15.7$$

$$b = 0.175$$

$$r = 1.000$$

for the fresh KI solution, indicating that ozone was the only oxidizing agent present.

The contents of the second impinger was used as a check of the amount of ozone not trapped by the first impinger. Iodine concentrations in the second impinger were found to be 0-2.4% of those in the first impinger.

Ozonized oxygen was generated with a Welsbach ozonator, using Linde tank oxygen. The settings on the Welsbach were as follows:

Pressure :  $8.0 \pm 0.2$  psi

Power : 90 volts

Flow Rate:  $0.60 \pm 0.05$

Calibration of the flow meter indicated that a rate of 0.60 corresponds to 0.34 liters/minute. In order to produce a constant ozone flow, the ozonator was conditioned by making ozone for at least twenty minutes before the reactant sample was collected.

The ozonolysis chamber was a teflon bag, constructed from a running roll of teflon film with a thermal impulse sealing device. A quick-connect fitting allowed easy access to the gaseous contents of the bag. The teflon film is relatively inert to most classes of chemicals and is clear, facilitating the detection of possible aerosol ozonolysis products.

Prior to actual ozone-olefin runs, the rate of decomposition of ozone in the teflon bag due to surface catalysis was assessed. The appropriate amount of ozonized oxygen was gas-injected into the bag and diluted with Linde Hydrocarbon-free Grade air to make a sample containing about 9 ppm  $O_3$ . The boric acid buffered KI analysis method was used to follow the decay of ozone with no olefin present over a period of twenty hours. A plot of  $\ln ([O_3]_t / [O_3]_0)$  as a function of time (Figure 3), resulted in a straight line, indicating first-order decay. The slope of this line gives the rate constant for ozone decay, which was used to calculate the halflife of ozone with no olefin present:

$$\text{slope} = -k_1$$

$$k_1 = 1.49 \times 10^{-3} \text{ min}^{-1}$$

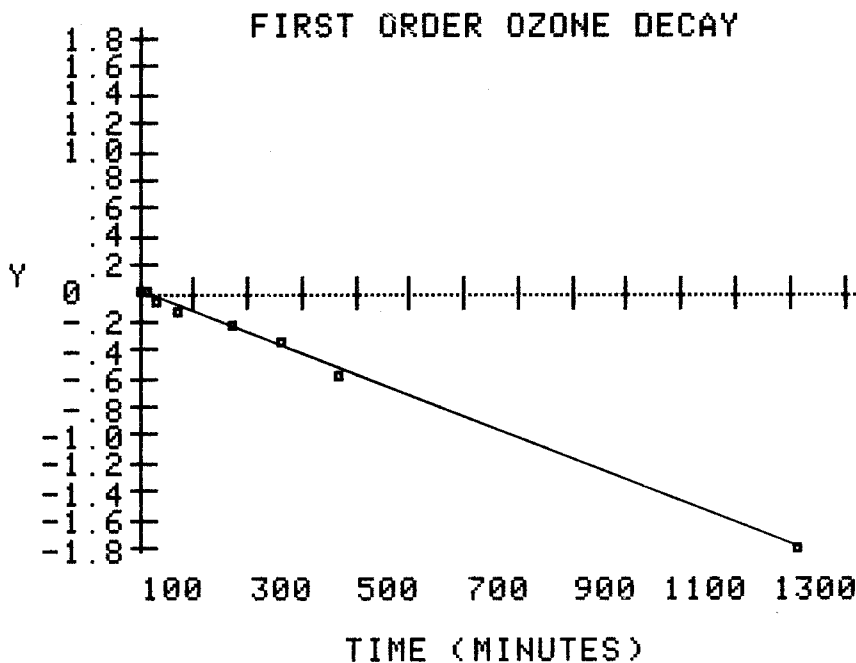
$$t_{1/2} = 465 \text{ min} = 2.79 \times 10^4 \text{ seconds}$$

The experimental rate of ozone decay in the teflon bag was found to be comparable with values reported in a previous study.<sup>57</sup>

The halflife of the tetramethylethylene-ozone reaction was estimated for the  $[olefin] = 25 \text{ ppm}$  case, using a pseudo first-order rate law approximation:

$$k_2 = 9 \times 10^{15} \text{ liters/mole-sec}^{92}$$

Figure 3:  
First-order Decay of Ozone in the Absence of Olefin



$$Y = \ln ([O_3]_t / [O_3]_0)$$

$$m = 1.49 \times 10^{-3}$$

$$b = 7.73 \times 10^{-3}$$

$$r = -0.9993$$

$$t_{1/2} \approx 4 \text{ seconds}$$

The difference in the halflife of ozone in the presence and absence of olefin ensures that essentially all of the ozone in the reaction mixture was available to react with tetramethylethylene.

#### b) Ozonolysis Experiments

The technique used in the experiments consisted of preparing the desired concentration of each reactant in a separate teflon bag, and then forcing the contents of one bag into the other. Mixing of the reactants was completed in approximately two minutes. All experiments were performed at ambient temperature and pressure.

The rate of ozone production by the Welsbach ozonator was previously determined by J. Sawyer to be  $0.60 \pm 20\%$  mmoles/minute.<sup>93</sup> Based on the output of the ozonator, the amount of ozonized oxygen required for the ozone sample was calculated. This volume was gas-injected into a teflon bag and diluted to the appropriate volume with hydrocarbon-free air. After mixing well, the exact concentration of ozone in the reactant sample was determined by the buffered KI analysis method.

The olefin bag was prepared by metering in a known volume of hydrocarbon-free air and then injecting the proper amount of liquid tetramethylethylene, using a microliter

syringe. Masking tape was used to seal the syringe puncture hole. The area around the puncture hole was warmed with the hands and the bag contents were agitated to ensure complete vaporization and thorough mixing of the olefin sample.

The purity of the tetramethylethylene was checked by gas chromatography. Two small impurity peaks were observed, one about 3% and one about 1.4% of the alkene peak.

Each reagent sample contained 5 liters of air. The concentration of each reactant was calculated on the basis of the total reaction mixture (10 liters). In most cases, the concentrations of ozone and olefin were approximately equivalent. Initial concentrations ranged from 12.5 to 800 ppm. Olefin-rich and ozone-rich reaction conditions were generated by the method of addition. In one set of experiments, the contents of the ozone bag were forced into the olefin sample (olefin-rich conditions), while a second set involved the reverse addition (ozone-rich conditions). The reaction mixture was agitated during the addition process and checked for the possible formation of an aerosol.

#### c) GC Analysis

Reaction products were analyzed by gas chromatography, using a 10-foot Carbowax column and flame ionization detection. Gaseous samples were injected directly into a Perkin Elmer 900 gas chromatograph with settings as follows:

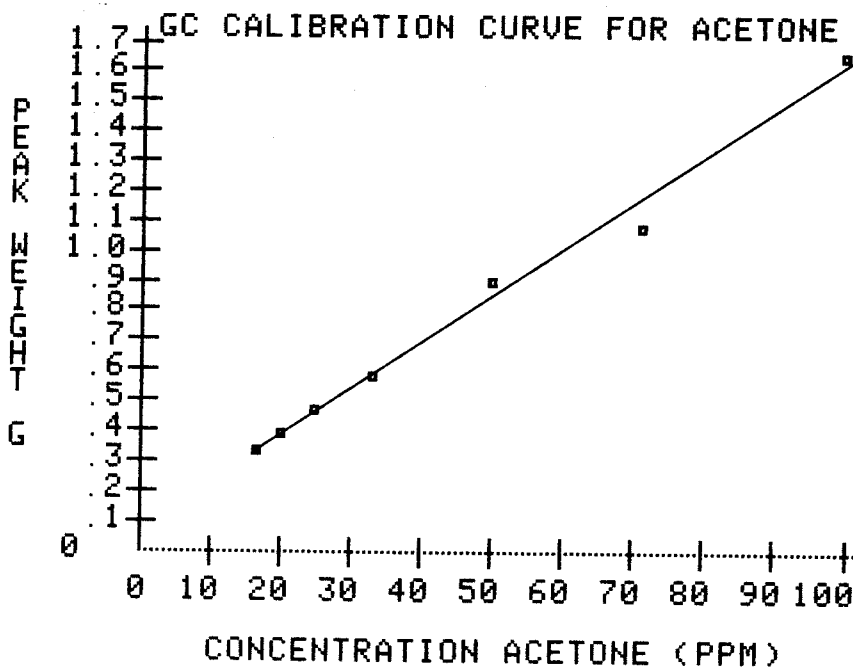
Carrier flow :  $3.0 \pm 0.2$   
Manifold temperature :  $200^{\circ} \text{C}$   
Injection port temperature:  $200^{\circ} \text{C}$

Each product mixture was analyzed at  $40^{\circ} \text{C}$  and  $150^{\circ} \text{C}$ . Attempts to combine the two analyses in a single temperature-programmed run proved to be unsuccessful because of the establishment of a temperature gradient in the column, which adversely affected sensitivity. The possible formation of peroxidic products which decompose at high temperatures was investigated by gc analysis with the injection port at room temperature.

Calibration data was collected for acetone, an expected product, and tetramethylethylene. A teflon bag containing a known concentration of these compounds in air was prepared and analyzed by gas chromatography. Sequential dilution gave additional concentration versus gc peak area data, which provided calibration curves for both compounds (Figures 4 and 5). These calibration curves were used to estimate the amount of acetone formed and the amount of unreacted tetramethylethylene remaining in each reaction mixture.

An attempt was made to identify additional ozonolysis products. Compounds which were reported in previous studies or predicted by the O'Neal-Blumstein mechanism were investigated as possible products. The following compounds were

Figure 4:



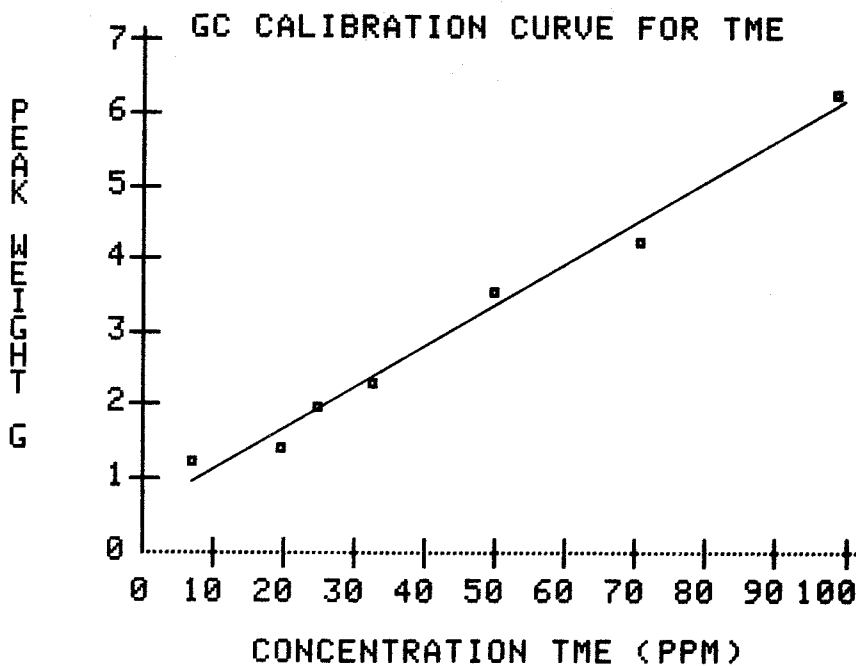
$$m = 1.53 \times 10^{-2}$$

$$b = 7.93 \times 10^{-2}$$

$$r = 0.9944$$



Figure 4:

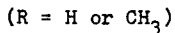
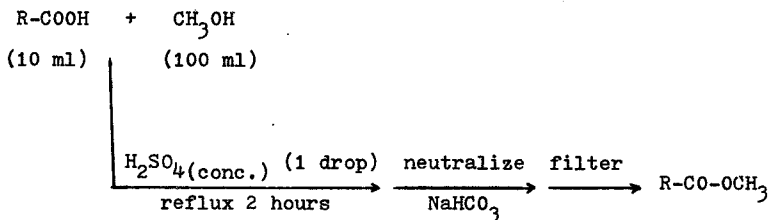


$$m = 5.62 \times 10^{-2}$$

$$b = 0.564$$

$$r = 0.9928$$

considered: formic acid, acetic acid, methanol, n-propyl alcohol, isopropyl alcohol, acetol, methyl formate, and methyl acetate. Commercially available samples of these compounds were analyzed, except in the case of methyl formate and methyl acetate, which were synthesized. The esters were prepared as follows:



## RESULTS AND DISCUSSION

This study is intended to provide insight into the mechanism of gas phase ozonolysis of olefins by considering the products of the reaction of ozone with tetramethylethylene. First the results of gc analysis of product mixtures and attempts to identify the products are reported. Changes in the stoichiometry of the ozonolysis reaction as a function of concentration and method of addition are discussed in terms of the O'Neal-Blumstein mechanism for gas phase ozonolysis. Finally, the results of this study are compared with previous work at higher concentrations.

Table 3 lists the results of gc analysis of the products of the ozonolysis of tetramethylethylene. The experiments are divided into two groups: those involving the addition of ozone to the olefin sample (olefin-rich conditions) and those involving the reverse addition (ozone-rich conditions). The initial reactant concentrations, amount of tetramethylethylene consumed, and amount of acetone formed are listed for each experiment. Ozone concentrations which are underlined in this table are approximate; in these runs, the exact concentration of the ozone reactant sample was not determined.

Concentrations and gc retention times at 40° C of products other than acetone are listed in column 3. The concentrations of these additional products are based on the ace-

tone calibration curve, and are therefore approximate. Most product mixtures also included several other peaks for which concentration values could not be determined. Retention times for these peaks are not listed in Table 3.

The stoichiometry of each experimental run is expressed in the form of three concentration ratios: acetone formed per olefin consumed, acetone formed per ozone consumed, and olefin consumed per ozone consumed. Values in column 4 which are underlined are somewhat uncertain because they are based on approximate initial ozone concentrations.

A number of aspects of the data summarized in Table 3 are worthy of further attention:

- a) Several compounds besides acetone are produced in the gas phase ozonolysis of tetramethylethylene.
- b) Within each set of experiments, the stoichiometry of the reaction varies with respect to initial concentrations.
- c) The method of addition (olefin into ozone or vice versa) has a dramatic influence on the ozonolysis product mixture.

Each of these observations will be considered in detail.

Table 3:

Results of GC Analysis of Product Mixtures Obtained in the Ozonolysis of Tetramethylethylene

Run	<u>Initial Conc.</u>		<u>Final Conc.</u>		<u>Other Products</u>		<u>Stoichiometry Ratios</u>		
	(ppm)		(ppm)		Conc. (ppm)	Retention Time (minutes)	<u>Acetone Formed</u>	<u>Acetone Formed</u>	<u>Olefin Reacted</u>
	O <sub>3</sub>	Olefin	Olefin Reacted	Acetone Formed			<u>Olefin Reacted</u>	<u>Ozone Reacted</u>	<u>Ozone Reacted</u>
1	12.5	25	20.6	8.7	1.3	1.2	0.42	0.70	1.65
					0.2	1.7			
2	32.6	25	23.0	36.4	7.8	1.5	1.58	1.12	0.71
					4.1	7.2			
3	<u>50</u>	50	44.6	40.6	7.8	1.3	0.91	<u>0.8</u>	<u>0.9</u>
4	<u>100</u>	100	82.6	79.6	16.3	1.2	0.96	<u>0.8</u>	<u>0.8</u>
5	<u>100</u>	100	97.4	87.2	24.2	1.5	0.90	<u>0.9</u>	<u>1.0</u>
					12.0	2.4			
					4.2	4.4			
6	167	200	130	198	36.4	1.1	1.52	1.19	0.78
					40.4	1.4			
					24.5	5.3			

Run	<u>Initial Conc.</u>		<u>Final Conc.</u>		<u>Other Products</u>		<u>Stoichiometry Ratios</u>		
	(ppm)		(ppm)		Conc. (ppm)	Retention Time (minutes)	<u>Acetone Formed</u>	<u>Acetone Formed</u>	<u>Olefin Reacted</u>
	O <sub>3</sub>	Olefin	Olefin Reacted	Acetone Formed			<u>Olefin Reacted</u>	<u>Ozone Reacted</u>	<u>Ozone Reacted</u>
7	<u>200</u>	200	109	158	41.6	1.5	1.45	<u>0.8</u>	<u>0.6</u>
					33.1	1.8			
					15.3	2.0			
					8.0	2.5			
					35.7	3.0			
					35.0	3.4			
					35.3	6.9			
					72.7	10.1			
8	<u>400</u>	400	231	432	77.2	1.4	1.87	<u>1.1</u>	<u>0.6</u>
					57.6	2.3			
					79.4	2.7			
					8.2	3.8			
					70.9	5.4			
					1.2	10.7			
					20.0	12.8			

Run	<u>Initial Conc.</u>		<u>Final Conc.</u>		<u>Other Products</u>		<u>Stoichiometry Ratios</u>		
	O <sub>3</sub>	Olefin	(ppm)		Conc. (ppm)	Retention Time (minutes)	<u>Acetone Formed</u> <u>Olefin Reacted</u>	<u>Acetone Formed</u> <u>Ozone Reacted</u>	<u>Olefin Reacted</u> <u>Ozone Reacted</u>
9	670	800	617	990	44.5 7.1	5.5 10.3	1.60	1.48	0.92
10	45	50	44.0	15.3	--	--	0.35	0.34	0.97
11	86	100	74.5	25.8	--	--	0.35	0.30	0.87
12	163	200	144.6	38.3	2.5 1.3 2.7 72	5.2 8.0 11.4 13.8	0.27	0.24	0.89
13	426	400	354.6	55.1	6.0 12.2 17.5	3.8 7.0 11.3	0.16	0.13	0.83
14	792	800	690.1	67.0	1.3 18.2 1.2	3.7 7.0 8.1	0.097	0.085	0.87

a) Identification of ozonolysis products

Gas chromatographic analysis indicated that the product mixture for each run had several components. In addition to the products whose concentrations are reported in column 3 of Table 3, most runs included some product peaks that could not be calibrated. An attempt was made to identify the components of the ozonolysis product mixture by comparison with the retention times of products which are predicted by the O'Neal-Blumstein mechanism. Table 4 summarizes the results of gas chromatographic analysis of some compounds which are suspected to be ozonolysis products.

Table 4:

Results of GC Analysis of Some Suspected Ozonolysis Products

<u>Compound</u>	<u>Retention Time (min)</u>	
	<u>40°C</u>	<u>150°C</u>
formic acid	0.6 1.3	0.3
acetic acid	---	1.7
methanol	1.5	---
n-propyl alcohol	2.4	0.4
isopropyl alcohol	1.2	0.3
acetol	---	1.6
methyl formate	0.6	---
methyl acetate	0.9	---



It was not possible to identify the ozonolysis products by comparison of their retention times with those of the authentic compounds. The complexity of the identification process is best illustrated by considering one of the experimental runs. Table 5 lists the product peaks observed when approximately 400 ppm  $O_3$  was forced into 400 ppm of tetramethylethylene (run 13).

Table 5:

Results of GC Analysis of Run 13 (400 ppm  $O_3$  + 400 ppm Olefin)

GC Column Temperature ( $^{\circ}C$ )	Retention Time (min)	Concentration (ppm)
40	0.7	169 (T)
40	1.1	432 (A)
40	1.4	77.2
40	2.3	57.6
40	2.7	79.4
40	3.8	8.2
40	5.4	70.9
40	10.7	1.2
40	12.8	20.0
150	3.5	30.9
150	11.3	124

(T) - tetramethylethylene

(A) - acetone

The first two peaks were positively identified as unreacted tetramethylethylene and acetone by spiking in an earlier run. GC retention times for these two compounds were found to vary by as much as  $\pm 0.2$  minutes. If this error margin is assumed to apply for all of the product peaks, none of the compounds which are listed in Table 4 are ruled out as possible components of the product mixture in this experimental run. Conversely, none of the ozonolysis products in Table 5 can be positively identified solely on the basis of comparison of gc retention times.

Several components of the product mixture for run 13 have retention times significantly higher than any of the compounds considered as possible products in Table 4. These peaks probably correspond to higher molecular weight ozonolysis products, which move through the polar carbowax column more slowly than the one-, two-, and three-carbon compounds considered in Table 4. GC analysis indicated that such components (with retention times varying from 3 to about 14 minutes at  $40^{\circ}\text{C}$ ) were present in most experimental runs. It is possible that species predicted by the O'Neal-Blumstein mechanism, such as peroxides, epoxides, or cyclic compounds, are among these products. Due to the complexity of the ozonolysis product mixture, gas chromatographic analysis can provide little more than preliminary information. Positive identification of products would require a more sensitive analytical method, such as mass spectrometry.

- b) Changes in stoichiometry as a function of initial reactant concentrations.

The majority of previous gas phase ozonolysis studies listed in Table 2 focus on the products observed for a single pair of initial concentrations. Only three studies report relative product yields at several initial concentrations. In two of the studies,<sup>11,33</sup> changes in initial reactant concentrations were reported to have no effect on the relative product yields. However, the conclusion that the composition of the product mixture is independent of the concentration of reactants used was based solely upon comparison of infrared spectral data, and is therefore somewhat suspect as to its validity. A single study which utilized gc analysis showed a change in the distribution of products over a range of initial reactant concentrations in the ozonolysis of allene.<sup>60</sup>

Although this investigation of the ozone-tetramethylethylene reaction did not succeed in the positive identification of major products, the results still provide insight into the O'Neal-Blumstein mechanism for gas phase ozonolysis. The experiments are grouped into two sets, according to the method of addition employed. In each set, changes in the stoichiometry of the ozonolysis reaction with respect to concentration are noted, and possible mechanistic explanations are offered.

Experimental runs 1-9 involved the addition of ozone to the olefin sample. It is difficult to interpret the results of this set in terms of a single, unified trend because the exact ratio of initial ozone and olefin concentrations varies markedly in some cases (runs 1 and 2) and is not accurately known in other cases (runs 3-5, 7, and 8). However, information which is valuable in terms of the O'Neal-Blumstein mechanism is obtained when certain subsets within this group of experiments are considered.

In runs 1 and 2, the concentration of the olefin sample was held constant while the initial ozone concentration was varied. The stoichiometry of the ozonolysis reaction appears to change dramatically as a function of the amount of ozone added. However, the results of the first two runs must be regarded as somewhat tentative, since they were not substantiated by repetitive experiments under similar conditions.

The concentration of ozone was significantly less than the concentration of olefin in the first run and significantly greater than the olefin concentration in the second run. Due to the method of addition, both of these experimental runs occurred in olefin-rich conditions (the amount of ozone entering the olefin bag at any instant was small in comparison to the amount of olefin present.) Therefore, run 2 involved the addition of an excess amount of ozone to the olefin sample such that the olefin was always present in excess. This

situation cannot be interpreted in terms of having a single reagent in excess.

Although no definite conclusions about the mechanism of ozonolysis can be drawn on the basis of runs 1 and 2, comparison of the results listed in Table 3 produces some interesting observations:

- 1) The amount of tetramethylethylene consumed is essentially constant in the two runs, regardless of the amount of ozone added.
- 2) In run 2, some olefin remained unreacted, even though the total amount of ozone added was larger than the initial olefin sample. This indicates that the "extra" ozone does not react with the olefin, but instead attacks one or more of the ozonolysis products.
- 3) The yield of acetone per tetramethylethylene consumed in run 2 is greater than triple that of run 1. It appears that the biradical formed in the Criegee split pathway may produce additional acetone via reaction with itself or other species in the product mixture. Another possible source of acetone could be reaction of the additional ozone in run 2 with an initial ozonolysis product. The latter explanation is the more plausible of the two, since it also accounts for the fact that the "extra" ozone in run 2 does not appear

to consume tetramethylethylene (observations 1) and 2) above).

Comparison of the runs involving addition of the ozone sample to an olefin sample of approximately equivalent concentration (runs 3-9) provides more insight into the mechanism of ozonolysis. Replicate runs were performed at two initial concentrations (100 ppm and 200 ppm). The stoichiometric ratios for two runs at the same initial concentration were about the same (allowing for some uncertainty concerning the concentration of the ozone sample), indicating that the results are reproducible. Over the concentration range 50-800 ppm, the stoichiometry of the reaction appears to vary as a function of the initial reactant concentrations:

1) Low concentrations (runs 3-5):

- a) The amount of acetone formed is approximately equal to the amount of tetramethylethylene consumed (0.9). In the O'Neal-Blumstein mechanism, the biradical formed by homolysis of a molozonide O-O bond may participate in the Criegee split pathway, yielding acetone. Since nearly one mole of acetone is produced for each mole of olefin that reacts, the Criegee split appears to be the major reaction pathway at low initial reactant concentrations.

- b) About 1:1 ozone-to-olefin stoichiometry is observed. This suggests that the reaction between ozone and the olefin predominates. Since approximately equal amounts of ozone and olefin are consumed, other reactions involving ozonolysis intermediates or products and one of the initial reactants are assumed to be minimal.

2) Higher concentrations (runs 6-9):

- a) The yield of acetone per tetramethylethylene jumps to about 1.5. As in run 2, this could be caused by reaction of the Criegee split biradical with itself or some other ozonolysis product, generating more acetone.
- b) Ozone could be involved in the production of additional acetone at higher concentrations: in runs 3-5, the ratio of olefin consumed per ozone reacted is about 0.9, and drops to about 0.6 in most higher concentration runs. This indicates that additional  $O_3$  is consumed in processes not directly involving tetramethylethylene. However, correlation between increased consumption of ozone and greater acetone yields at higher concentrations is not without exception. The experiment involving 800 ppm of each reactant (run 9) produced anomalous results, consisting of a high acetone yield coupled with nearly

1:1 olefin-to-ozone stoichiometry. Therefore, the role of ozone in the production of additional acetone in higher concentration olefin-rich conditions is not clear.

Definite stoichiometric trends are evident in runs 10-14, which involved forcing the olefin into the ozone sample. In these experiments, the ratio of tetramethylethylene consumed remained constant (within experimental error) at a little less than 1:1 in terms of ozone present. This implies that the mode and rate of attack of ozone on the olefin (the initial reaction of the O'Neal-Blumstein mechanism, leading to the formation of the molozonide) is essentially the same over this concentration range. One-to-one stoichiometry indicates that the ozonolysis reaction is proceeding via primary attack of ozone on the olefin; that is, various forms of secondary attack which have been postulated in some previous work<sup>10,45,48</sup> do not appear to be operative under these conditions.

O'Neal and Blumstein postulated the next step in the ozonolysis process to be a ring-opening reaction, yielding a biradical species which may then participate in a variety of possible hydrogen abstraction pathways leading to the final products. In the case of tetramethylethylene, acetone is formed as a result of the Criegee split reaction. Therefore, the ratio of acetone formed per ozone reacted may be



considered as a measure of the favorability of the Criegee split possibility, in comparison to all other reaction pathways.

In the ozone-rich set of experiments (runs 10-14), the ratio of acetone per  $O_3$  starts out at a low value of about 0.3 and then drops by two-thirds over the concentration range 50 ppm to 800 ppm. If the acetone present in the ozonolysis product mixture is assumed to arise only from the Criegee split pathway, the trend in runs 10-14 could indicate a relative disfavoring of that reaction possibility with increasing initial concentrations. Within the framework of the O'Neal-Blumstein proposal, such an observation would be interpreted as a relative favoring of the various abstraction processes that the biradical (produced by O-O bond cleavage in the molozonide) may undergo. This possible explanation could be tested by further analysis of the ozonolysis product mixture, in an effort to find compounds which are predicted as final products in abstraction pathways of the O'Neal-Blumstein mechanism.

The ozonolysis scheme proposed by O'Neal and Blumstein rationalizes the change in the yield of acetone with respect to addition method as a difference in the relative favorability of the various pathways in olefin-rich and ozone-rich reaction conditions. However, this explanation offers little information about the observed concentration dependence within

each set of experiments. Since every pathway available to the oxy-peroxy biradical in the O'Neal-Blumstein mechanism is unimolecular (involving either cleavage or intramolecular hydrogen abstraction), one would expect the distribution of the biradical between the Criegee split and abstraction pathways to be concentration-independent. As a result, the yield of acetone per olefin consumed would be constant over the concentration range in each set of ozonolysis experiments. Contrary to the prediction of the O'Neal-Blumstein mechanism, both sets of ozonolysis experiments are concentration-dependent. The proposed disfavoring of the Criegee reaction was found to increase as a function of initial reactant concentrations in an ozone-rich environment (runs 10-14) and to decrease as a function of initial concentration in an olefin-rich environment (runs 3-9).

Several sources indicate that a portion of the carbonyl products formed in gas phase ozonolysis reactions are initially "bound" as peroxides.<sup>11,33,34,45,53,56,78,79</sup> These compounds are thermally unstable, and therefore often decompose during the analysis procedure. It is possible that such peroxide intermediates were formed in the ozonolysis of tetramethylethylene. These highly reactive species would decompose on the gc column, yielding more stable carbonyl products (probably including acetone) in their "free" state. The stable compounds which are identified by gc analysis are recognised as the final ozonolysis products.

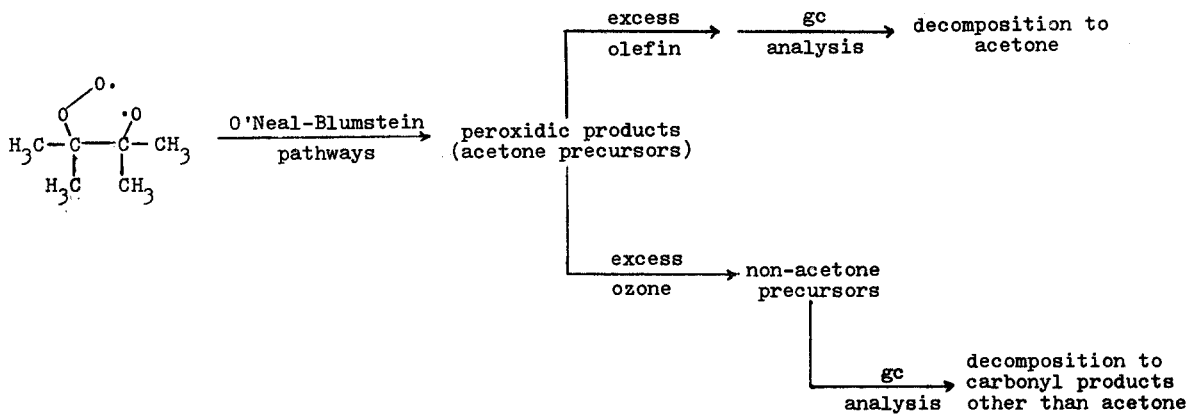
The environment in which these peroxide intermediate species are produced could determine what stable form they will appear in after they decompose on the gc column. Suppose that peroxide intermediates are formed in the gas phase ozonolysis of tetramethylethylene. If these species are acetone precursors in their initial form, and if conditions are sufficiently mild to prevent further reaction, the decomposition products which are obtained as a result of gc analysis will include acetone. However, peroxidic ozonolysis products are quite unstable, and would be expected to react further in more vigorous conditions.

In the olefin-rich experiments (runs 3-9), any peroxidic products would be formed in an environment composed mainly of tetramethylethylene. It is possible that conditions in this set of runs would be mild enough to preclude further reaction of such intermediates. If the initial peroxidic species formed were acetone precursors, subsequent decomposition due to gc analysis would result in a product mixture with a sizable acetone component. However, any "bound" carbonyl products formed in the experiments involving the reverse addition (olefin forced into ozone) are subjected to reaction conditions which are more oxidizing, due to the excess ozone present throughout most of the reaction. If these peroxidic intermediates undergo further reaction, leading to non-acetone precursors, the yield of acetone as determined by gc analysis would be much smaller (Scheme 5).

Scheme 5:

Possible Fates of "Bound" Carbonyl Products in Olefin-rich and Ozone-rich Environments

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This reaction pathway may explain the dramatically lower yield of acetone in ozone-rich conditions. Peroxidic products which are acetone precursors could react further in the presence of excess ozone, producing non-acetone precursors which decompose during analysis to yield stable products other than acetone. Direct attack of ozone on any peroxide intermediates seems unlikely, since the ratio of tetramethylethylene reacted per ozone in runs 10-14 indicates that nearly all of the ozone is involved in attack at the olefinic double bond. Consumption of ozone in processes not directly involving tetramethylethylene would alter the observed 1:1 reaction stoichiometry.

It is possible that the proposed conversion of peroxidic intermediates to non-acetone precursors could occur via a free-radical chain reaction which is initiated by ozone. This sort of process could consume an insignificant amount of ozone, and therefore have no effect on the olefin-to-ozone stoichiometry. The existence of an  $O_3$  catalyzed free-radical conversion pathway would also account for the decrease in acetone yields with increasing initial reactant concentrations. In the higher concentration ozone-rich experiments, more ozone is present to initiate such a process. If a chain reaction ensues, resulting in the conversion of "bound" carbonyl species produced in the ozonolysis process from acetone precursors to other forms, the amount of acetone

released in gc analysis would be expected to decrease with increasing reactant concentrations.

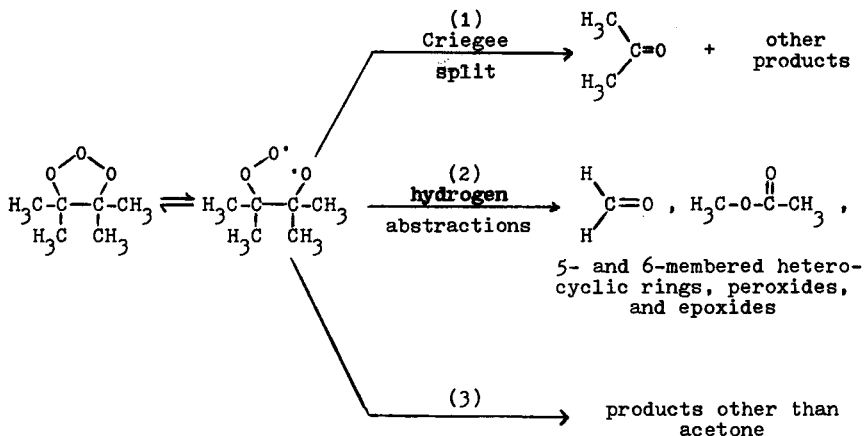
Alternative explanations for the decrease of the amount of acetone formed with increasing initial reactant concentrations in the ozone-rich set of experiments should not be ruled out. The experimental work leading to the O'Neal-Blumstein proposal for gas phase ozonolysis<sup>10,11,33,34,53,55,57,78,79,94</sup> involved olefin-rich reaction conditions. Without exception, the reaction vessel was filled with the vaporized olefin, and then ozone was allowed to stream slowly into the olefin sample. Consequently, the O'Neal-Blumstein mechanism for gas phase ozonolysis presumes olefin-rich reaction conditions. Since runs 10-14 took place in an ozone-rich environment, it is conceivable that processes totally different from those proposed by O'Neal and Blumstein occurred.

The decrease in the yield of acetone with increasing reactant concentrations in ozone-rich conditions may indicate the existence of alternative pathways in the ozonolysis mechanism, leading to products not predicted by O'Neal and Blumstein. These additional pathways, whose effects would be minimal in the normal olefin-rich situation, may compete or even predominate in determining the fate of the oxy-peroxy biradical in ozone-rich conditions. It is possible that the biradical produced by homolysis of an O-O bond in the

primary ozonide reacts in an entirely different way if excess ozone is present:

Scheme 6:

Proposed Alternative Pathway(s)  
in the O'Neal-Blumstein Ozonolysis Mechanism for Tetramethylethylene



Path (3) may involve reaction of the oxy-peroxy biradical with ozone or peroxidic ozonolysis intermediates, producing carbonyl species other than acetone. The possible favorability of this pathway in ozone-rich reaction conditions would reduce the amount of biradical available to participate in the Criegee split and various hydrogen abstrac-

tion pathways, and thus possibly diminish the amount of acetone in the ozonolysis product mixture.

Reaction of the biradical with ozone or peroxides could also account for the concentration dependence observed in runs 10-14. Acetone yields were found to decrease with increasing initial reactant concentrations. If ozone-rich conditions favored pathway (3), the presence of excess ozone would result in reducing the total amount of biradical available to react via ordinary O'Neal-Blumstein processes. Consequently, the formation of products predicted by O'Neal and Blumstein, notably acetone, would be suppressed. The relative disfavoring of paths (1) and (2) would increase at higher concentrations, resulting in even smaller acetone yields.

- c) Changes in the stoichiometry of the reaction with respect to the method of addition.

Traditionally, ozonolysis studies have focused upon excess-olefin conditions, in which the ozone was allowed to stream slowly into the olefin sample. Runs 10-14 investigate an entirely different aspect of the ozonolysis reaction, in which the method of addition results in ozone-rich conditions. Comparison of the product mixtures obtained for each addition method (ozone forced into olefin and vice versa) can elucidate differences in the ozonolysis mechanism in excess-olefin and excess-ozone environments. Runs



3-9 are representative of ozonolysis under olefin-rich conditions, while runs 10-14 illustrate the ozone-rich case.

1) Olefin:ozone stoichiometry:

The ratio of tetramethylethylene/ozone consumed is approximately unity for all ozone-rich runs, and also the low concentration olefin-rich runs (3-5). In some of the olefin-rich experiments at higher concentration (runs 6-8) the observed olefin:ozone stoichiometry was somewhat lower than 1:1 (about 0.6). A stoichiometric ratio of less than one indicates that ozone is being consumed in processes which do not directly involve the olefin. It is possible that some ozone reacts with initial ozonolysis products in the higher concentration olefin-rich experiments. Attack of ozone on products or intermediates appears to be minimal in the ozone-rich runs, since the ratio of olefin consumed per ozone remains essentially constant at a little less than unity (0.83-0.97) over the concentration range 50-800 ppm.

2) Acetone yields:

The amount of acetone produced as a result of ozonolysis in an olefin-rich environment increases as a function of initial reactant concentrations. In contrast, acetone yields in experiments involving the addition of tetramethylethylene to ozone (ozone-rich conditions) exhibit inverse dependence on reactant concentrations and are overall much

lower than in the excess-olefin situation. Part b) in this section proposes three possible mechanistic interpretations of the low yield of acetone observed in ozone-rich ozonolysis:

- i) Relative disfavoring of the Criegee split pathway in excess-ozone conditions (fails to account for the observed concentration dependence within each set of ozonolysis experiments.)
- ii) Formation of peroxidic intermediates (acetone precursors) which undergo conversion processes in the presence of excess ozone. (Scheme 5)
- iii) Existence of one or more reaction pathways not predicted by O'Neal and Blumstein, which become operative in an ozone-rich environment. (Scheme 6)

The results of this study of the ozonolysis of tetramethylethylene are not sufficient to draw definite conclusions about the validity of proposals ii) and iii). Future experimental work should include further investigation of these mechanistic possibilities.

- d) Comparison to previous work.

Table 6 lists the results of previous studies involving the ozonolysis of tetramethylethylene. Initial reactant concentrations, the amount of olefin reacted, the diluent gas

Table 6:

## Results of Previous Studies of the Ozonolysis of Tetramethylethylene

Ref.	<u>Initial Conc.</u>		Olefin Reacted (ppm)	Diluent	Total Pressure (mm Hg)	Analysis Method	Reported Products	<u>Stoichiometry Ratios</u>		
	O <sub>3</sub>	Olefin (ppm)						Acetone Formed Olefin Reacted	Acetone Formed Ozone Reacted	Olefin Reacted Ozone Reacted
48	8,000	17,000	All	N <sub>2</sub> + O <sub>2</sub>	760	Chemical Analysis  IR	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> COOH H <sub>2</sub> CO HCOOH CH <sub>3</sub> OH CH <sub>3</sub> OCOCH <sub>3</sub> significant aerosol formation	0.132	---	>2
45	4,900	29,000	All	O <sub>2</sub>	110	GLC	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> significant aerosol formation	---	1.45	2.0

Ref.	<u>Initial Conc.</u>		Olefin Reacted (ppm)	Diluent	Total Pressure (mm Hg)	Analysis Method	Reported Products	<u>Stoichiometry Ratios</u>		
	O <sub>3</sub>	Olefin (ppm)						<u>Acetone Formed Olefin Reacted</u>	<u>Acetone Formed Ozone Reacted</u>	<u>Olefin Reacted Ozone Reacted</u>
45	4,900	29,000	All	N <sub>2</sub>	110	GLC	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> slight aerosol formation	---	0.65	~1
56	10,000	30,000	All	O <sub>2</sub>	110-440	GLC	CH <sub>3</sub> COCH <sub>3</sub> CO <sub>2</sub> HCOOH CH <sub>3</sub> CHO CH <sub>3</sub> OCHO CH <sub>3</sub> OH C <sub>3</sub> H <sub>6</sub> peroxidic intermediates	---	1.49	---
54	~0.01	17,800	920	O <sub>2</sub>	760	IR	CH <sub>3</sub> COCH <sub>3</sub> H <sub>2</sub> CO	---	---	---
53	3,250	52,000	All	O <sub>2</sub>	110-135	GLC	CH <sub>3</sub> COCH <sub>3</sub>	---	---	---

used, the total pressure of the reaction mixture, and the method of analysis are included. Reported products are listed in order of decreasing yield. The product column also includes information about the possible formation of peroxidic intermediates or aerosol components. The table also includes any stoichiometric ratios reported for the ozonolysis reaction.

All of the studies listed in table 6 were at significantly higher initial reactant concentrations (except for a single case in which the ozonolysis reaction was used to monitor a steady-state ozone concentration.<sup>54</sup>) The results of previous work provide an interesting comparison with those obtained in the concentration range 10-800 ppm. Several aspects of high and low concentration results are examined, and then the data is discussed in terms of the modelling of atmospheric ozonolysis reactions.

1) Aerosol formation:

Two previous studies reported the formation of a significant amount of aerosol in the gas phase ozonolysis of tetramethylethylene.<sup>45,48</sup> In this study, each reaction mixture was checked visually for cloudiness which would indicate the presence of particulate matter. A small amount of aerosol was observed in the 800 ppm ozone-rich experiment (run 14). Aerosol formation does not appear to be favored in low concentration ozonolysis reactions.

## 2) Peroxide formation:

Peroxidic intermediates were reported as components of the ozonolysis product mixtures in a single study involving tetramethylethylene.<sup>56</sup> The presence of these unstable species was indicated by a positive KI test performed on the reaction mixture prior to chromatographic analysis.

In this study, the possible formation of peroxidic products which decompose at high temperatures was investigated by gc analysis with the column at 40° C and the injection port at room temperature. Comparison to gc analysis with the injection port at 200° C showed that no additional products were detected at the lower injection port temperature. Since a preliminary test for peroxides (prior to gc analysis) was not performed, the possible presence of such intermediates in the low-concentration reaction mixtures cannot be ruled out.

The possibility of peroxidic species present in the ozonolysis product mixture is an important concern, since it may provide insight into the relative validity of suggestions ii) and iii) (offered in explanation of the acetone yields observed in the ozonolysis of tetramethylethylene.) Proposal ii) hypothesizes the formation of peroxidic acetone precursors which are converted to other forms in the presence of excess ozone. The detection of peroxides in the ozonolysis product mixture would not constitute proof that the proposed conversion is actually occurring, but such an

observation would suggest the existence of pathways involving peroxidic species.

### 3) Stoichiometry

Comparison of the stoichiometry of the ozonolysis of tetramethylethylene at high concentration (Table 6) and at low concentration (Table 3) results in some interesting observations:

#### i) Olefin:ozone stoichiometry:

The ratio of tetramethylethylene consumed per ozone is much greater for the high concentration ozonolysis process. In previous work, the consumption of more than one molecule of olefin per molecule of ozone was rationalized by attack of biradical species or peroxide intermediates on the olefin.<sup>45,48</sup> These forms of attack do not appear to occur in the absence of molecular oxygen<sup>45</sup> or at low initial reactant concentrations (Table 3), since the observed olefin:ozone stoichiometry is 1:1 or less. An alternative explanation of the change in the ratio of olefin consumed per ozone would be the generation of additional ozone at higher concentrations (perhaps via a free-radical chain reaction.) The additional ozone would increase the consumption of olefin, resulting in greater than 1:1 stoichiometry.

#### ii) Acetone formed/olefin consumed:

The previous high concentration studies listed in Table

6 all involved the addition of ozone to the olefin sample (olefin-rich conditions). These results would be expected to be comparable with the lower concentration experiments involving the same method of addition (runs 1-9).

A single ozonolysis study expressed the yield of acetone in terms of olefin consumed.<sup>48</sup> The value reported in this high concentration study is significantly lower than any of the acetone/olefin results for experiments involving the addition of the ozone sample to an equivalent amount of tetramethylethylene (runs 3-9). It is interesting to note that the value within the low-concentration olefin-rich set which corresponds most closely to the acetone/olefin ratio reported at high concentrations is that of run 1. Both run 1 and the high concentration study involved the addition of an ozone sample to an olefin sample which was twice as large. Although these two studies differ vastly in initial concentrations, the stoichiometry ratios reported for run 1 and for reference 48 show general agreement:

	<u>Acetone formed</u> <u>olefin</u>	<u>Olefin consumed</u> <u>ozone</u>
low concentration (run 1)	0.42	1.65
high concentration (reference 48)	0.132	2.

This observation may imply that the relative size of the



reactant samples has a more pronounced effect on the ozonolysis mechanism than does the overall concentration of the reactant mixture.

iii) Acetone formed/ozone consumed:

Two high concentration studies reported acetone:ozone stoichiometry ratios for the ozonolysis of tetramethylethylene.<sup>45,56</sup> These results are compared with the corresponding olefin-rich experiments at low concentrations (runs 3-9).

At the low end of the concentration range studied (runs 3-5), acetone yields are far below those reported in high concentration work. In contrast, the amount of acetone produced per ozone in the higher concentration experiments of this set (runs 6-9) approaches the values reported in the literature.<sup>45,56</sup> Significant changes in acetone yields over the concentration range 10-800 ppm could indicate fundamental differences in the ozonolysis mechanism as a result of initial reactant concentrations.

4) Modelling of atmospheric ozonolysis processes.

In the past, several attempts have been made to explore the mechanism of degradation of organic molecules in the atmosphere.<sup>11,41,49,95-101</sup> Current efforts focus on determining the atmospheric fate of organic toxic substances by assessing the individual effects of various chemical and physical removal processes.<sup>44,50-52,102,103</sup> Both rates and prod-

ucts of degradative reactions are being studied. It is hoped that continued research will make it possible to piece together the available information to form a cohesive understanding of atmospheric chemistry.

Reaction with ozone constitutes one of three major pathways of chemical degradation of organic molecules in the atmosphere.<sup>34,41,50-52,104</sup> Therefore, the ozonolysis of organic molecules has commanded ever-increasing interest in the field of atmospheric chemistry. On the basis of measured compositions of smoggy atmospheres<sup>105</sup> and the rate constants for the reaction of ozone with various species contained in such atmospheres, it has been concluded that, under typical atmospheric conditions, the primary carbon-containing species involved in ozone-related removal processes are olefins.<sup>102</sup> Consequently, an understanding of the mechanism of gas phase ozonolysis of olefins is of great importance in the modelling of atmospheric systems.

The validity of any model in explaining a natural process is limited by the accuracy of the experimental work upon which it is based. Most product representations of atmospheric ozone-olefin reactions have depended upon data collected at fairly high reactant concentrations, since the bulk of previous product research in gas phase ozonolysis has involved concentrations of several thousand ppm. (Table 2). These experimental results were assumed to be valid

when extrapolated to the low reactant concentrations which prevail in atmospheric systems.

The results of this study of the ozonolysis of tetramethylethylene suggest that work done in the concentration range of several thousand ppm may not be valid in the modelling of atmospheric ozonolysis processes. The products and relative stoichiometry of the ozonolysis reaction were found to be significantly different than previous results which involved higher initial reactant concentrations. In addition, the ozonolysis mechanism appeared to change quite dramatically over the concentration range 10-800 ppm. It is likely that the actual ozonolysis process which is occurring at ambient atmospheric concentrations of ozone (recently estimated to be about  $0.04 \text{ ppm}^{106}$ ) cannot be approximated by high concentration studies.

### SUGGESTIONS FOR FUTURE WORK

#### a) Improvements of Analytical Procedures

In this study of the ozonolysis of tetramethylethylene, gc analysis was utilized mainly for determining the amount of unreacted olefin remaining in the reaction mixture and the amount of acetone formed. The ozonolysis product mixture was found to contain several components other than acetone, but none of these compounds were positively identified. Obviously, the gc analysis procedure was not developed to its fullest potential in investigating the products of gas phase ozonolysis.

Variations in gc retention times of expected and actual products from day to day introduced a large amount of uncertainty which complicated the identification of components of the ozonolysis mixture. In the future, this problem could be avoided by standardizing the retention times of expected products as part of the analysis procedure. A teflon bag containing authentic samples of several compounds which are anticipated as ozonolysis products could be prepared and analyzed under exactly the same gc conditions as the reaction mixture. Component peaks of the ozonolysis mixture could then be compared with gc data for authentic samples analyzed under the same conditions. This standardization technique would minimize the uncertainty of gc product analysis caused by variations in retention times.

Several additional compounds which are predicted as products of the Criegee split or hydrogen abstraction pathways should be considered as possible components of the ozonolysis mixture. Also, compounds reported as products in previous ozonolysis studies involving tetramethylethylene should be investigated. Ethane, ethanol, methane, acetaldehyde, and propene are some possibilities.

The ozonolysis product mixture should be tested for the presence of peroxidic intermediates prior to gc analysis. A previous study<sup>56</sup> employed a KI test for this purpose. The ozone analysis method, which involves the oxidation of I<sup>-</sup> to I<sub>2</sub>, would probably be applicable to analysis for peroxides. Knowledge of the presence or absence of these species would be valuable in the consideration of alternative explanations for the inverse concentration dependence of acetone yields in ozone-rich reaction conditions (Schemes 5 and 6).

Alternative analysis methods should be employed for possible products which cannot be detected by gas chromatographic analysis. Methane, carbon dioxide, carbon monoxide, and especially formaldehyde should be considered. Detection of the presence of formaldehyde is particularly important in terms of the O'Neal-Blumstein mechanism, since it is predicted as an ozonolysis product of tetramethylethylene. (Scheme 4, path G; formaldehyde arises from oxy- $\beta$ -hydrogen

abstraction followed by ring closure to a 4-membered 1,2-dioxetane ring which subsequently cleaves.) As more ozonolysis products are identified, the relative favorability of O'Neal-Blumstein and other pathways can be considered further.

The application of gc/mass spectrometric techniques in analysis of the product mixture would be particularly advantageous. GC/MS product identification would be more dependable than comparison of retention times. In addition, this technique may provide information about peroxidic products which would be valuable in understanding the mechanism of ozonolysis.

b) Reaction conditions which merit further study:

- 1) The anomalous results obtained in runs 1 and 2 seem to indicate that the relative sizes of the olefin and ozone samples have a major effect on the relative favorability of various ozonolysis pathways. Further experiments varying the relative sample sizes would provide more insight into this observation.
- 2) A previous high concentration study<sup>45</sup> involved the use of nitrogen rather than oxygen or air as a diluent gas. This work could be duplicated at lower initial reactant concentrations, providing additional information about the course of the ozonolysis reaction in the absence of molecular oxygen.

- 3) Experiments involving equal amounts of olefin and ozone (as in runs 3-9 and 10-14) should be extended to higher and lower concentrations. Higher concentration studies would be important for comparison with previous work, while ozonolysis at lower reactant concentrations would be significant in the modelling of atmospheric systems.

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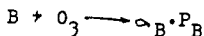
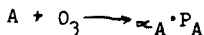


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84. Product yields are given as the number of moles of product per mole of olefin consumed.
85. The numerical value for the yield results from a competitive reaction:



The yield for olefin A is  $\alpha_A/\alpha_B$ ; the yield for olefin B is  $\alpha_B/\alpha_A$ .

86. Less than 10% trans isomer.
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