Oxidation of Haloethylenes

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I. Introduction

Since the publication of an earlier review[1] of the literature on the gas-phase oxidation of perhalocarbons, new and more extensive data, particularly on the simple halocarbons which shed light on their general oxidation mechanisms, have been reported. Also, there has developed recently a serious concern that some of the commonly used halocarbons may adversely affect the ozone concentration in the stratospheric layer surrounding our planet.[2-4] It is appropriate, therefore, to review at this time the oxidation reactions of another class of these halocarbons, namely, the haloethylenes. We examine here the existing experimental data and their interpretations for the reactions of haloethylenes with atomic oxygen and with ozone.

II. Cl-Atom-Initiated Oxidation

The chlorine-atom-initiated oxidation of chloro- and chlorofluoroethylenes has been studied in our laboratory.[5-9] Previously the chlorine-atom-initiated oxidation of C_2Cl_4,[10-13] C_2HCl_3,[14-16] and CHClCHCl[17] had been studied. The oxidation of CCl_2CCl_2, $CHClCCl_2$, CH_2CCl_2, *cis*-CHClCHCl, *trans*-CHClCHCl, CF_2CCl_2, and CFClCFCl (mixed cis and trans) proceeds by a long-chain free-radical process. The major products are the corresponding acid chlorides containing one or two carbon atoms. By contrast there is no chain process in $CHClCH_2$. The oxidation products and chain lengths are summarized in Table I. Also included in Table I are some preliminary results[18] on the chlorine-atom-initiated oxidation of CF_2CF_2 and CF_2CFCl. These oxidations also involve long-chain reactions. For most of the chloroethylenes, the chain length of the reaction exceeds 100 at sufficiently high O_2 pressures and is independent of the absorbed light intensity, I_a, or any of the reactant pressures.

The generalized mechanism which explained both the chlorination and oxidation was elucidated by Huybrechts et al.[13,15,19] In their studies of the photochlorination of $CClHCCl_2$ at 363 and 403 K, they found that small amounts of oxygen inhibited the photochlorination, but that the reaction proceeded further in the dark after irradiation was terminated.[19] They interpreted this after-effect to be due to the formation of a semistable peroxide which decomposes in the dark on the walls of the reaction vessel to reinitiate the chain chlorination.

Further studies of the photooxidation of $CClHCCl_2$[15] completed the earlier work of Müller and Schumacher[14] and showed that the principal oxidation product was $CCl_2HCCl(O)$ which accounted for ≥90% of the oxidation at 363 K and ≥82% of the oxidation at 403 K. Likewise they studied the chlorine-sensitized photooxidation and the simultaneous oxygen-inhibited photochlorination of CCl_2CCl_2 and C_2HCl_5 at 353.5 and 373.4 K. Both systems produced C_2Cl_5 radicals as the chain carrier. The results of the two systems were the same and nearly identical with those of Schumacher et al;[12,20] 85 ± 5% of the oxidized CCl_2CCl_2 and C_2HCl_5 appeared as $CCl_3CCl(O)$ and 15 ± 5% as CCl_2O. Trace quantities of CCl_4 (0.3%) and tetrachloroethylene oxide (0.1%) were also present. The quantum yield of oxidation, $\Phi\{OX\}$, increased with the oxygen pressure to an upper limiting value of about 300 for C_2Cl_5 radical oxidation and about 200 for $CHCl_2CCl_2$ oxidation, independent of absorbed intensity, I_a, chlorocarbon pressure, Cl_2 pressure, or added N_2 pressure. Huybrechts et al.[13,15] emphasized the different light-intensity dependency in the quantum yields for the oxygen inhibited chlorination ($I_a^{-1/2}$) and the high O_2 pressure limiting oxidation (intensity independent). They showed that since these two reactions are coupled they have common chain-breaking steps, which must be bimolecular in radicals to explain the $I_a^{-1/2}$ dependence of the quantum yield of chlorination. This led them to propose the following general mechanism:

$$Cl_2 + h\nu \rightarrow 2Cl \tag{1}$$

$$Cl + CX_2CXCl \rightarrow ClCX_2CXCl \tag{2a}$$

$$\rightarrow CX_2CXCl_2 \tag{2b}$$

$$ClCX_2CXCl + O_2 \rightarrow ClCX_2CXClO_2 \tag{3}$$

$$CX_2CXCl_2 + O_2 \rightarrow CXCl_2CX_2O_2 \tag{3'}$$

$$2ClCX_2CXClO_2 \rightarrow 2ClCX_2CXClO + O_2 \tag{4a}$$

$$\rightarrow (ClCX_2CXClO)_2 + O_2 \tag{4b}$$

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TABLE I. Chlorine-Atom Sensitized Oxidation of $C_2Cl_{4-n}H_n$ and $C_2Cl_{4-n}F_n$

Compound	Oxidation products (%)	$\Phi\{OX\}$[a]	k_{2a}/k_{2b}[b]	k_4/k_{4b}	k_{6a}/k_{6b}[c]	Ref[d]	Log k_2,[e] $M^{-1}\ s^{-1}$
CCl_2CCl_2	$CCl_3CCl(O)$ (75), CCl_2O (25)	300[f]	1	150	6.0	5,13	10.1
CCl_2CHCl	$CHCl_2CCl(O)$ (90), CO, CCl_2O	200[f]	~10	100	>6	15,16	10.6
CCl_2CH_2	$CH_2ClCCl(O)$ (98), CO, CCl_2O	172	$\gtrsim$100	86	>50	6	
cis-CClHCClH	CHClO (71), CO (26), CCl_2O (3)[g]	21.5	1	19	<50	7	10.6
trans-CClHCClH	CHClO (71), CO (26), CCl_2O (3)[g]	21.5	1	19	<50	7	10.6
$CClHCH_2$	CHClO (74), CO (25)[h]	~2	>10				
CF_2CCl_2	$CClF_2CCl(O)$ (91) CCl_2O (4), CF_2O (4)	~85	≥20		>22	9	
CFClCFCl[i]	$CCl_2FCF(O)$ (~100)	420	1	210	>50	9	
$CClFCF_2$	$CClF_2CF(O)$ (~95)	>1000	>10		>20	18	
CF_2CF_2	CF_2O (100)	~250	1		<0	18	

[a] $\Phi\{OX\} = -\Phi\{olefin\}$, neglecting isomerization. [b] Calculated from product distribution. [c] At 30–32 °C. [d] Reference for k_{6a}/k_{6b}. [e] From ref 23. [f] At high O_2 pressure. [g] In these olefins, geometrical isomerization of the starting olefin is an important process especially at low total pressure. [h] At high $[O_2]/[Cl_2]$ ratios. [i] Equilibrium mixture of cis and trans isomers.

TABLE II. Bond Energies (kcal/mol) in Chloroethoxy Radicals[a]

RO	$D\{C–H\}$[b]	$D\{C–Cl\}$[b]	$D\{C–C\}$[c]	$D\{C–Cl\} - D\{C–C\}$	k_{6a}/k_{6b}
CCl_3CCl_2O		−17	−20	+3	6.0
CCl_2HCCl_2O		−16	−13	−3	>6.0
CCl_3CHClO	6	−4	−16	+12	<10
$CClH_2CCl_2O$		−20.8	−11.6	−9.2	>50
CCl_3CH_2O	17		11		. . .[c]
$CCl_2HCHClO$	6	−5	−11	+6	<50
$CClH_2CHClO$	2	−4	−8	+4	<10
CCl_2HCH_2O	14.8		7		. . .[d]

[a] The values are mostly from ref 24. [b] $D\{C–H\}$ and $D\{C–Cl\}$ represent the bond energies for loss of H or Cl, respectively, from the oxygen-bearing carbon atom. [c] Neither of the products $CCl_3CH(O)$ nor CH_2O was observed experimentally ($k_{2a}/k_{2b} \geq 100$). [d] Neither of the products $CHCl_2CH(O)$ nor CH_2O was observed experimentally.

$$2CXCl_2CX_2O_2 \rightarrow 2CXCl_2CX_2O + O_2 \tag{4a'}$$

$$\rightarrow (CXCl_2CX_2O)_2 + O_2 \tag{4b'}$$

$$ClCX_2CXClO_2 + ClCX_2CXCl \rightarrow (ClCX_2CX_2ClO)_2 \tag{5}$$

$$ClCX_2CXClO \rightarrow ClCX_2CX(O) + Cl \tag{6a}$$

$$\rightarrow CXClO + ClCX_2 \tag{6b}$$

$$CXCl_2CX_2O \rightarrow CXCl_2CX(O) + X \tag{6a'}$$

$$\rightarrow CXCl_2 + CX_2O \tag{6b'}$$

$$ClCX_2 + O_2 \rightarrow CX_2O + Cl + \tfrac{1}{2}O_2 \tag{7a}$$

Reaction 7a, of course, is not a fundamental reaction but must proceed through several steps, which presumably are:

$$ClCX_2 + O_2 \rightarrow ClCX_2O_2$$

$$2ClCX_2O_2 \rightarrow 2ClCX_2O + O_2$$

$$ClCX_2O \rightarrow CX_2O + Cl$$

However there is an alternative to reaction 7a that could account for the oxidation in which the ClO radical is an intermediate but in which $ClCX_2O$ is not:

$$ClCX_2 + O_2 \rightarrow CX_2O + ClO \tag{8}$$

$$ClO + CX_2CXCl \rightarrow CX_2ClCXClO \tag{9}$$

Mathias et al.[5] tested the two possibilities. They examined the chlorine-atom-sensitized oxidation of C_2Cl_4 in the presence of O_3 to ensure that ClO was produced via the well-established rapid reaction[21]

$$Cl + O_3 \rightarrow ClO + O_2 \tag{10}$$

With O_3 present, the epoxide., $\overline{CCl_2CCl_2O}$, was produced. The epoxide does not come from the direct ozonolysis reaction since that reaction is completely suppressed in the presence of excess O_2, as discussed later. Since the epoxide production depended on the ratio $[C_2Cl_4]/[O_3]$, it was concluded that the epoxide came from

$$C_2Cl_4 + ClO \rightarrow \overline{CCl_2CCl_2O} + Cl \tag{11a}$$

No epoxide was produced in the absence of O_3, so presumably ClO radicals are absent, and reaction 7a is the correct representation of the oxidation of CCl_3 radicals.

From the experiments of Huybrechts et al.[13,15] and Mathias et al.[5] reaction 7a was established for CCl_3 radicals. In order to examine the oxidation of partially chlorinated methyl radicals, Sanhueza and Heicklen[22] examined the chlorine-atom-sensitized oxidation of CH_2Cl_2 and CH_3Cl to study the oxidation of $CHCl_2$ and CH_2Cl, respectively. They found that $CHCl_2$ oxidized just like CCl_3, but that CH_2Cl oxidation did not generate the chlorine atom. Presumably the oxidation of this radical is analogous to that for CH_3 radicals.

$$ClCH_2 + O_2 \rightarrow CHClO \text{ via termination} \tag{7b}$$

In the CCl_2CCl_2 and $CHClCCl_2$ systems, the quantum yields of oxidation products increased with the O_2 pressure until upper limiting values were reached. The mechanism predicts that if termination is exclusively by reaction 5, then

$$\Phi\{OX\} = \left(\frac{2k_3{}^2k_4}{k_5{}^2}\right)^{1/3}\left(\frac{[O_2]^2}{I_a}\right)^{1/3} \tag{I}$$

However if termination is exclusively by reaction 4b, then

$$\Phi\{OX\} = 2k_4/k_{4b} \tag{II}$$

where $\Phi\{OX\} \equiv -\Phi\{olefin\} = \Phi\{ClCX_2CCl(O)\} + \tfrac{1}{2}\Phi\{CX_2O\} + \tfrac{1}{2}\Phi\{CO\}$. Equation I applies at low values of $[O_2]^2/I_a$, whereas eq II applies at high values of $[O_2]^2/I_a$.

In the oxidation of CH_2CCl_2, *cis*-CHClCHCl, *trans*-CHClCHCl, and CFClCFCl the quantum yields of the oxidation products are insensitive to all the reaction parameters, and the termination must be by reaction 4b exclusively; eq II always applies. However, in the oxidation of CCl_2CH_2, since CH_2Cl always is oxidized in a nonchain process, reaction 6b′ also can be a terminating step.

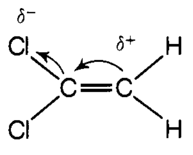
In the oxidation of CF_2CCl_2 there is one striking difference from the results of the other chloro- and/or fluoroethylenes: $\Phi\{CF_2ClCCl(O)\}$ is reduced at high pressure, but $\Phi\{CF_2O\}$ is not. Thus the details of the mechanism contain some additional subtle deviation from the general mechanism outlined above. A possible explanation is given in detail in the original work.[9]

In Table I the experimental results are summarized, and in

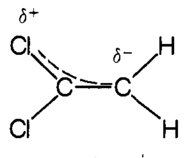
Table II the bond energies of the chloroethoxy radicals involved in the process of oxidation of the chloroolefins are presented. From Tables I and II it is possible to deduce the following information:

(1) From the values of k_{2a}/k_{2b} (obtained mainly from the distribution of products), it is possible to conclude that the chlorine atom prefers to attack the less chlorinated carbon atom. In the most unsymmetrical cases (CCl_2CH_2 and CCl_2CF_2), the preference for the nonchlorinated carbon atom is at least a factor of 20. The chloro olefins with one or three chlorine atoms also show a high preference for substitution on the less chlorinated carbon atom. In particular this was demonstrated for CCl_2CHCl by Bertrand et al.[16] at 357 K, who found the preference for chlorine-atom addition to the less chlorinated carbon atom to be at least eight times greater than for addition to the more chlorinated one. They did this by comparing the products of the reaction with those produced from the photochlorinated oxidation of CH_2ClCCl_3 (to produce CCl_3CClH) and $CHCl_2CHCl_2$ (to produce CCl_2HCCl_2). Of course, the symmetrical chloroethylenes can show no preference, and k_{2a} and k_{2b} are indistinguishable.

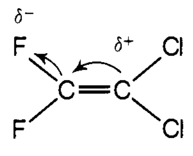
The inductive (I^-) and mesomeric (M^+) effects of the three substituent atoms are F > Cl > H. If these effects dominated the chlorine-atom addition, then H and F substitution should give different results. However, the chlorine atom always prefers to add to the less chlorinated carbon atom. Thus we conclude that steric effects must dominate the addition process.



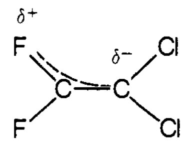
inductive



mesomeric



inductive



mesomeric

(2) A long-chain oxidation (>150) occurs when the exothermicity of either reaction 6a or 6b is greater than 11 kcal/mol. For an exothermicity of 11 kcal/mol, a relatively short-chain length (~20) is involved.

(3) In $CHClCH_2$, the radical produced is $CH_2ClCHClO$, and the exothermicity of decay of this radical by any route is <11 kcal/mol. The favored route to decay (most exothermic) is by C–C cleavage which produces the terminating radical CH_2Cl. Thus one cannot be certain that the parent radical would, of itself, lead to short chains.

(4) The reaction

$$ClCX_2CXHO \rightarrow ClCX_2CX(O) + H$$

is always energetically less favorable than the cleavage of either the C–C bond or the oxygenated carbon–chlorine bond. There was no evidence that this reaction occurred in any of the systems studied.

(5) In radicals of the type CX_3CH_2O, all the decomposition routes are sufficiently endothermic so that no decay products are observed. Thus in the oxidation of CCl_2CH_2 no CH_2O or $CCl_3CH(O)$ was found as products, and in the oxidation of $CHClCH_2$, no $CHCl_2CH(O)$ or CH_2O was found as products.

(6) When $D\{C–Cl\} - D\{C–C\}$ is ≥6 kcal/mol, almost all the chlorinated ethoxy radical decomposition goes through reaction 6b. When $D\{C–Cl\} - D\{C–C\} < -3$ kcal/mol, almost all the decomposition proceeds through reaction 6a. For intermediate values of the bond energy difference, both reaction paths are significant.

(7) The chlorine-atom-initiated oxidation of all the perfluorochloroolefins ($C_2F_{4-n}Cl_n$) which have been studied gives long chains. No study has been made for $CClFCCl_2$, but there is no reason to believe that its oxidation will not proceed through a long-chain process.

(8) In the mixed chlorofluoroethylenes, the products are almost entirely (>90%) the two-carbon acid chloride. Thus we would expect that $D\{C–Cl\} - D\{C–C\} < -3$ kcal/mol in the ethoxy radical precursor. This observation can be compared with the results for *cis*- and *trans*-$CHClCHCl$, where no two-carbon carbonyl compounds were found. Thus the substitution of F for H either strengthens the C–C bond or weakens the oxygen-bearing carbon–chlorine bond or both.

(9) In C_2F_4, the two-carbon carbonyl compound is missing. Thus we conclude that the C–F bond is stronger than the C–C bond in the ethoxy radical, whereas in CX_3CXClO the carbon–chlorine bond is weaker than the C–C bond.

A. Vinyl Chloride

The chlorine-atom-sensitized oxidation of $CHClCH_2$ is unique among the chloro olefin oxidations for three reasons: (1) CO is produced as a major initial product of the reaction, the ratio $[CO]/[CHClO]$ being almost independent of reaction parameters; (2) there is no chain at high values of the ratio $[O_2]/[Cl_2]$; and (3) at low values of $[O_2]/[Cl_2]$, there is a long-chain process which consumes Cl_2 and produces $CH_2ClCCl(O)$ as the principal chain product.

The production of CO as an initial product is explained by a slight extension of reaction 6

$$CH_2ClCHClO \rightarrow CH_2Cl + CO + HCl \qquad (6c)$$

where reaction 6c probably proceeds through an energetic $CHClO$ molecule which always decomposes. Reaction 6b to produce $CHClO$ as a product still occurs but represents that fraction of reaction 6 in which the $CHClO$ produced is stabilized. The same results were found in the $CHClCHCl$ oxidation.

The lack of a chain reaction at high $[O_2]/[Cl_2]$ pressures is the result of the fact that reaction 6a does not occur and that reactions 6b and 6c produce the terminating radical CH_2Cl. Presumably the termination reaction 7b occurs via the sequence of steps[22]

$$CH_2Cl + O_2 \rightarrow CH_2ClO_2$$

$$2CH_2ClO_2 \rightarrow 2CH_2ClO + O_2$$

followed by

$$CH_2ClO_2 + CH_2ClO \rightarrow 2CHClO + H_2O$$

or

$$CH_2ClO + O_2 \rightarrow CHClO + HO_2$$

$$CH_2ClO_2 + HO_2 \rightarrow CHClO + H_2O + O_2$$

The production of $CH_2ClCCl(O)$ and the dependence of the results on the Cl_2 pressure represent findings not seen in any other chloroethylene and which were explained[8] by the competition:

$$CH_2ClCHCl + O_2 \rightarrow CH_2ClCHClO_2 \qquad (3)$$

$$CH_2ClCHCl + Cl_2 \rightarrow CH_2ClCCl_2 + HCl \qquad (12)$$

where reaction 12 is then followed by oxidation to produce $CH_2ClCCl(O)$ as it does in the CH_2CCl_2 system. The competition between reactions 3 and 12 leads to the rate law

$$\Phi\{CH_2ClCCl(O)\} = k_{12}[Cl_2]/k_3[O_2] \qquad (III)$$

since ultimately reaction 12 regenerates the chain. A log–log plot of $\Phi\{CH_2ClCCl(O)\}$ vs. $[O_2]/[Cl_2]$ is shown in Figure 1. It is fitted reasonably by a straight line of slope −1. The intercept

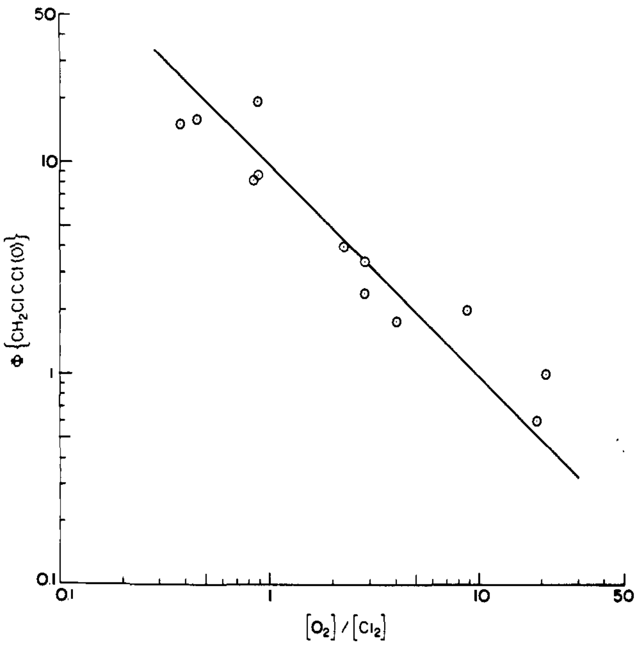


Figure 1. Log-log plot of $\Phi\{CH_2ClCCl(O)\}$ vs. $[O_2]/[Cl_2]$ in the chlorine-atom-initiated oxidation of C_2H_3Cl at 31 °C. From Sanhueza and Heicklen[8] with permission of the American Chemical Society.

yields a value for $k_{12}/k_3 = 9.5$.

Confirmation that the chlorine-atom-initiated oxidation of $CClHCH_2$ does not lead to a chain process comes from the work of Bertrand et al.[24] who studied the chlorine-atom-initiated oxidation of 1,2-$C_2H_4Cl_2$ at 353 K to produce $CClH_2CClH$. Furthermore they showed that chloroethyl radicals not chlorinated on the α-carbon do not lead to chain oxidations by examining the chlorine-atom-initiated oxidation of C_2H_4 (to produce $CClH_2CH_2$) and CCl_3CH_3 (to produce CCl_3CH_2). Earlier work[25] on the chlorine-atom-initiated oxidation of C_2H_6 had shown that C_2H_5 also does not enter a chain oxidation.

B. O_3 Present

The chlorine-atom-initiated oxidation of C_2Cl_4 was studied in the presence of O_3, since the dark reaction for this system was very slow.[5] The addition of O_3 to the system introduced three major changes:

(1) The ratio $\Phi\{CCl_3CCl(O)\}/\Phi\{CCl_2O\}$ dropped as the $[O_3]/[O_2]$ ratio was increased but was unaffected by changes in $[O_3]/[C_2Cl_4]$. The effect of the $[O_3]/[O_2]$ ratio is seen in Figure 2. There is considerable scatter in the data, but at 32° the ratio drops from about 3.0 in the absence of O_3 to about 1.0 at $[O_3]/[O_2] > 10$. The data points at 24 °C lie below those at 32 °C, as they do in the absence of O_2. The shift in the ratio was attributed to the production of $CCl_3CCl(O)$ and CCl_2O via

$$C_2Cl_5 + O_3 \rightarrow CCl_3CCl(O) + Cl + O_2 \quad (13a)$$

$$\rightarrow CCl_2O + CCl_3O_2 \text{ (or } CCl_3 + O_2) \quad (13b)$$

where the ratio k_{13a}/k_{13b} is smaller than k_{6a}/k_{6b}. It was argued[5] that reactions 13a and 13b proceeded directly and not through energetic $C_2Cl_5O^*$ radicals, since the thermal effect was known to move the product ratio in the opposite direction.[5]

(2) The overall rate of the oxidation was reduced as the $[O_3]/[C_2Cl_4]$ ratio was raised. This was attributed to the production of ClO radicals via reaction 10 followed by the competition of C_2Cl_4 and O_3 for ClO. Most of the time that ClO reacted with O_3, the chain is regenerated

$$ClO + O_3 \rightarrow Cl + 2O_2 \quad (14a)$$

but occasionally termination might occur by

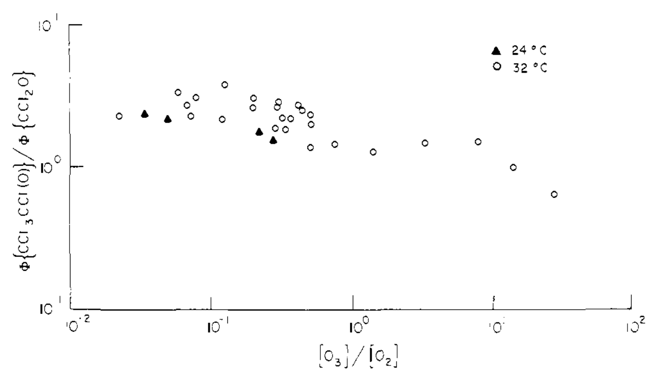


Figure 2. Log-log plot of the ratio of the quantum yields of $CCl_3CCl(O)$ and CCl_2O vs. $[O_3]/[O_2]$ in the chlorine-atom-sensitized oxidation of C_2Cl_4 by O_2 and O_3 at 32 °C. From Mathias et al.[5] with permission of the National Research Council of Canada.

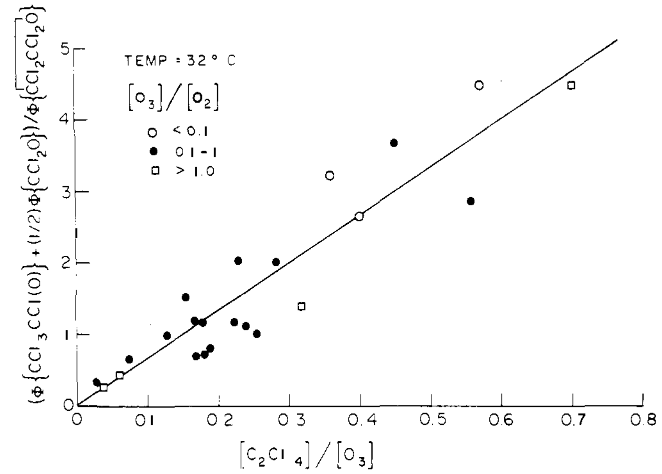


Figure 3. Plot of $(\Phi\{CCl_3CCl(O)\} + \frac{1}{2}\Phi\{CCl_2O\})/\Phi\{\overline{CCl_2CCl_2O}\}$ vs. $[C_2Cl_4]/[O_3]$ in the chlorine-atom-sensitized oxidation of C_2Cl_4 by O_2 and O_3 at 32 °C. From Mathias et al.[5] with permission of the National Research Council of Canada.

$$ClO + O_3 \rightarrow OClO + O_2 \quad (14b)$$

followed by subsequent oxidation of OClO to produce the observed product Cl_2O_7.

(3) Tetrachloroethylene oxide was produced, its quantum yield depending mainly on the $[C_2Cl_4]/[O_3]$ ratio. This result suggested that it was produced in the ClO–C_2Cl_4 interaction:

$$ClO + C_2Cl_4 \rightarrow \overline{CCl_2CCl_2O} + Cl \quad (11a)$$

$$\rightarrow CCl_3CCl(O) + Cl \quad (11b)$$

$$\rightarrow CCl_2O + CCl_3 \quad (11c)$$

Since the chain length was long under all conditions, the mechanism predicted that

$$\frac{\Phi\{CCl_3CCl(O)\} + \frac{1}{2}\Phi\{CCl_2O\}}{\Phi\{\overline{CCl_2CCl_2O}\}} = \frac{k_{11b} + k_{11c}}{k_{11a}} + \frac{k_2k_{14}}{k_{11a}k_{10}} + \frac{k_2k_{14}}{k_{10}k_{14a}}\frac{[C_2Cl_4]}{[O_3]} \quad (IV)$$

Figure 3 is a plot of the left-hand side of eq IV vs. $[C_2Cl_4]/[O_3]$, and it is seen that a straight-line plot passing through the origin is obtained. Thus reactions 11b and 11c are unimportant.

C. F_2-Initiated Oxidation

Miller and Dittman[26] passed mixtures of F_2 and O_2 into C_2Cl_4 or C_2F_3Cl at 0 °C. Presumably the oxidation is similar to that initiated by chlorine atoms. With C_2Cl_4 the products, in decreasing order of abundance were $CCl_3CCl(O)$, $CCl_2FCCl(O)$, CCl_2O, C_2Cl_6, and Cl_2. Trace amounts of $(CFCl_2)_2$ and C_2Cl_5F were also observed. With C_2F_3Cl the major product was $CF_2ClCF(O)$ with CFClO, CF_2O, and CF_3CFO also formed. The main feature of the two systems can be explained in terms of C_2Cl_4F and C_2F_4Cl oxidation, respectively.

III. Hg 6(^{3}P) Sensitization

The Hg-photosensitized oxidation of three chloro olefins (CCl_2CCl_2, $CHClCCl_2$, and CH_2CCl_2) have been studied in our laboratory.[6,27,28] For two of these olefins, the mercury-sensitization was also studied in the absence of O_2, and we will discuss these results first.

A. O_2 Absent

The Hg-photosensitized decompositions of CCl_2CCl_2[27] and $CHClCCl_2$[28] were studied. The results were similar in the two studies. The products were Hg_2Cl_2 and polymeric material. The quantum yield of olefin loss, $-\Phi\{CX_2CCl_2\}$ (X = H, Cl), was $\sim$1, independent of olefin pressure and nearly independent of absorbed intensity, I_a ($-\Phi\{CHClCCl_2\}$ appeared to be between 1.5 and 2.0 at low I_a). In the $CHClCCl_2$ study small amounts of another unidentified product were found.

The results indicate that a long-chain polymerization of the olefin is not involved, since $-\Phi\{CX_2CCl_2\} \simeq 1.0$. Double-bond cleavage can be eliminated since $c\text{-}C_3Cl_6$ was not produced in the CCl_2CCl_2 system and mixed ethylenes were not produced in the $CHClCCl_2$ system. Molecular elimination does not seem likely, and in fact the results with O_2 present eliminate that possibility as a major reaction path. It was concluded that free radicals must have been produced by one of the following processes:

$$\text{Hg }6(^3P) + CX_2CCl_2 \rightarrow C_2X_2Cl + \tfrac{1}{2}Hg_2Cl_2 \tag{15a}$$

or

$$\text{Hg }6(^3P) + CX_2CCl_2 \rightarrow \text{Hg }6(^1S) + CX_2CCl_2^* \tag{15b}$$

$$\text{Hg }6(^1S) + CX_2CCl_2^* \rightarrow C_2X_2Cl + \tfrac{1}{2}Hg_2Cl_2 \tag{16}$$

In the case of $CHClCCl_2$, the possibility also exists of producing C_2Cl_3 + H + Hg 6(^{1}S) as products, either directly or through the excited molecule mechanism. Presumably the C_2X_2Cl radical dimerizes, and the resulting 1,3-butadiene polymerizes.

The above mechanism to produce free radicals is markedly different from that for the Hg-photosensitized decomposition of the fluoroethylenes or C_2H_4. Ethylene and the fluoroethylenes (except for C_2F_4) decompose by molecular elimination of H_2[29] and HF,[30] respectively. C_2F_4[31-33] and to a slight extent trifluoroethylene[30b] decompose by double-bond cleavage.

For C_2F_4 the mechanism that explained the results was:

$$\text{Hg }6(^3P_1) + CF_2CF_2 \rightarrow \text{Hg }6(^1S_0) + (CF_2CF_2)_n^* \tag{15b'}$$

$$(CF_2CF_2)_n^* \rightarrow 2\ {}^1CF_2 \tag{17}$$

$$(CF_2CF_2)_n^* + CF_2CF_2 \rightarrow (CF_2CF_2)_0^* + CF_2CF_2 \tag{18}$$

$$(CF_2CF_2)_0^* \ (+\ CF_2CF_2) \rightarrow CF_2CF_2(+\ CF_2CF_2) \tag{19}$$

followed by

$$2\,{}^1CF_2 \rightarrow C_2F_4 \tag{20}$$

$${}^1CF_2 + C_2F_4 \rightarrow c\text{-}C_3F_6 \tag{21}$$

where the superscript * represents an electronically excited state, the subscripts n and 0 represent, respectively, molecules with either sufficient or insufficient energy to dissociate, and $^1CF_2$ is the singlet CF_2 diradical.

The rate coefficients for the quenching of Hg 6(^{3}P) by the olefins have been measured. Relative to N_2O they are 3.0 for C_2Cl_4,[27] 4.1 for $CHClCCl_2$,[29] 0.35 for C_2F_4,[1] and 1.8 for C_2H_4.[29]

B. O_2 Present

The Hg-photosensitized oxidation of C_2F_4 has been reported in two studies[33,34] and reviewed by Heicklen.[1] A complete mechanism has been presented and discussed in detail.[34] The products of the reaction were $c\text{-}C_3F_6$, CF_2O, and tetrafluoroethylene oxide.

The mechanism is very complex. However, the oxidation products can be explained as coming from the following reactions involving a diradical.

$$(C_2F_4)_0^* + O_2 \rightarrow CF_2O_2 + {}^1CF_2 \tag{22}$$

$${}^1CF_2 + C_2F_4 \rightarrow c\text{-}C_3F_6 \tag{21}$$

$$CF_2O_2 + C_2F_4 \rightarrow 2CF_2O + {}^3CF_3 \tag{23a}$$

$$\rightarrow CF_2O + \overline{CF_2CF_2O} \tag{23b}$$

$${}^3CF_2 + O_2 \rightarrow CF_2O_2 \tag{24}$$

Here $(C_2F_4)_0^*$ is a vibrationally equilibrated electronically excited C_2F_4 molecule; $^1CF_2$ and $^3CF_2$ are the singlet and triplet of CF_2 radical, respectively.

For the chloro olefins in the presence of O_2, a long-chain process occurs. The major products are the same as for the chlorine-atom-initiated oxidation of the corresponding chloro olefin, and these products are produced in the same ratio. There are two major differences for the two modes of initiating the oxidation.

(1) At high $[O_2]/I_a^{1/2}$ the quantum yields are independent of the reactant pressures and I_a for chlorine-atom initiation. For Hg 6(^{3}P) sensitization, at low $[O_2]/[CX_2CCl_2]$ (to minimize removal of Hg 6(^{3}P) by O_2), the quantum yields are independent of the O_2 pressure and I_a, but they increase proportionately with the chloro olefin pressure.

(2) CO is produced as an initial product from the Hg 6(^{3}P) sensitization but not from chlorine-atom initiation. (CO was found in the Cl + $CHClCCl_2$ + O_2, system,[15] but presumably it is a decomposition product of CHClO or formed through energetic CHClO as a precursor.)

The conclusions from the above observations are that the same free-radical chain process must occur in both systems, but that the initiation mechanism must be different. In order to explain the facts, Sanhueza and Heicklen[6,27,28] utilized the following mechanism for the Hg 6(^{3}P)-sensitized oxidation:

$$\text{Hg }6(^3P) + CX_2CCl_2 \rightarrow CX_2CCl_2^* + \text{Hg }6(^1S) \tag{15b}$$

$$\text{Hg }6(^3P) + O_2 \rightarrow O_2^* + \text{Hg }6(^1S) \tag{25}$$

$$O_2^* + CX_2CCl_2 \rightarrow CX_2CCl_2^* + O_2 \tag{26}$$

$$CX_2CCl_2^* + \text{Hg }6(^1S) \rightarrow C_2X_2Cl + \tfrac{1}{2}Hg_2Cl_2 \tag{16}$$

$$C_2X_2Cl + O_2 \rightarrow C_2X_2ClO_2 \tag{27}$$

$$C_2X_2ClO_2 \rightarrow \text{CO via termination} \tag{28}$$

$$C_2X_2ClO_2 + CX_2CCl_2 \rightarrow C_2X_2Cl_3 + (CXO)_2 \tag{29}$$

In the hydrogenated chloro olefins, the product yields decreased as $[O_2]/[CX_2CCl_2]$ increased beyond a certain value (4.0 for $CHClCCl_2$ and 1.8 for CH_2CCl_2). However, with C_2Cl_4 there was no decrease in the product yields even at $[O_2]/[C_2Cl_4] = 22$, in spite of the fact that quenching of Hg 6(^{3}P) by O_2 is only slightly less efficient than quenching by C_2Cl_4. Thus it was necessary to postulate that Hg 6(^{3}P) sensitization leads to the production of an excited olefin molecule, regardless of whether the olefin or O_2 quenched the Hg 6(^{3}P) atom. The same postulate was required in the C_2F_4 system.[1]

Presumably the free radical C_2X_2Cl adds O_2 and this radical must initiate the chain process. Since the chain process is

TABLE III. Rate Coefficient Ratios from the Hg 6(^{3}P) Sensitized Oxidation of Chloroethylenes at 30–32 °C

		Value for		
Ratio	Units	CCl_2CCl_2[a]	$CHClCCl_2$[b]	CH_2CCl_2[c]
k_{2a}/k_{2b}	None	1	6.7	. . .
k_{29}/k_{28}	$Torr^{-1}$	0.029	0.015	0.058

[a] From ref 27. [b] From ref 28. [c] From ref 6.

proportional to $[CX_2CCl_2]$, and initiation must be via reaction 29, the main removal process for $C_2X_2ClO_2$ must be by some process represented by reaction 28. Reaction 28 is, of course, not a fundamental process. In order for termination ultimately to occur, another radical must be involved. Possibly reaction 28 occurs on the wall of the reaction vessel. In any event it must produce the excess CO that is observed as a product.

The mechanism leads to the following rate laws:

$$\Phi\{CO\} = 1.0 \text{ for } CCl_2CCl_2 \text{ and } CH_2CCl_2 \qquad (V)$$

$$\Phi\{CO\} = 1.0 + \Phi\{CCl_2C\} \text{ for } CHClCCl_2 \qquad (V')$$

$$-\Phi\{CX_2CCl_2\} - 1 = (k_4k_{29}/k_{4b}k_{28})[C_2Cl_4] \qquad (VI)$$

$\Phi\{CO\}$ should be higher for $CHClCCl_2$ than for the other chloro olefins because no CHClO was found. Presumably it was formed "hot" and always decayed to CO + HCl. For the C_2Cl_4 system, $\Phi\{CO\}$ was unity in good agreement with expectation. In the CH_2CCl_2 system, $\Phi\{CO\}$ was somewhat low (0.5–1.0), but this probably reflects experimental uncertainty since CO is a minor product. However, in the $CHClCCl_2$ system, $\Phi\{CO\} - 1$ was larger than predicted by eq V′ by a factor of 4.6, and this extra CO has not been satisfactorily explained.

Table III summarizes the rate coefficient data obtained for the three olefins. The values of k_{29}/k_{28} are of the same order of magnitude in the three systems; the variation that does exist does not follow any trend.

It is interesting to compare the above results with those of the photooxidation of C_2F_3I[35] which produces C_2F_3, a radical analogous to C_2X_2Cl

$$C_2F_3I + h\nu \rightarrow C_2F_3 + I \qquad (30)$$

In this system a small chain occurred which produced CF_2O, CFIO, and C_2F_3OI as major products and $(CFO)_2CF_2$ and $(CFO_2)CF_2(CFO)$ as minor products. The latter products must involve CFO as a precursor and come from the oxidation of C_2F_3

$$C_2F_3 + O_2 \rightarrow CF_2O + FCO \qquad (31a)$$

The main chain steps considered were

$$C_2F_3 + O_2 \rightarrow C_2F_3O_2 \qquad (31b)$$

$$C_2F_3O_2 + C_2F_3I \rightarrow C_2F_3 + CF_2O + CFIO \qquad (32a)$$

$$\rightarrow C_2F_3OI + C_2F_3O \qquad (32b)$$

$$C_2F_3O + I \rightarrow C_2F_3OI \qquad (33)$$

Though Heicklen[35] did not consider them, additional chain steps are also possible through the iodine atom as chain carrier

$$I + C_2F_3I \rightarrow CF_2ICFI \qquad (34)$$

$$CF_2ICFI + O_2 \rightarrow CF_2ICFIO_2 \qquad (35)$$

$$2CF_2ICFIO_2 \rightarrow 2CF_2ICFIO + O_2 \qquad (36)$$

$$CF_2ICFIO \rightarrow C_2F_3OI + I \qquad (37a)$$

$$\rightarrow CFIO + CF_2I \xrightarrow{O_2} CF_2O + I \qquad (37b)$$

In fact, reaction 37a is needed to explain the high quantum yields (up to 10) of C_2F_3OI which were observed. Reactions 32b and 33 can only account for $\Phi\{C_2F_3OI\} \leq 2$. It should be noticed that C_2F_3OI ($F_2C{=}C(F)OI$) is the enol type isomer of $CF_2ICF(O)$, the molecule expected to be produced via reaction 37a if the system were exactly analogous to those of the chlorinated ethylenes.

Thus this system contains many analogous features of the Hg 6(^{3}P) sensitized oxidation of chloroethylenes. Reaction 31a is a termination step corresponding to reaction 27 followed by reaction 28, and reaction 31b followed by reaction 32a is a propagation step corresponding to reaction 27 followed by reaction 29.

IV. Reaction with O(^{3}P) Atoms

The oxygen atom might react with chloroethylenes by any of the following paths (X = H, F, Cl):

$$O(^3P) + CXClCX_2 \rightarrow CX_2O + CClX \qquad (38a)$$

$$\rightarrow CO + X_2 + CClX \qquad (38b)$$

$$\rightarrow CXClCX_2O^* \qquad (38c)$$

$$\rightarrow CX_2ClCX(O) \qquad (38d)$$

$$\rightarrow CClX_2 + XCO \qquad (38e)$$

where $CXClCX_2O^*$ represents several excited structures, including that of the epoxide. Each of the reaction paths actually represents only one of two possibilities, since the O(^{3}P) atom could attack either the more heavily or less heavily chlorinated carbon atom. However, we anticipate the results and show that the O(^{3}P) generally attacks the less chlorinated carbon atom in the chloroethylene.

The diradical CClX enters into one of two reactions.

$$2CClX \rightarrow CClXCClX \qquad (39)$$

$$CClX + CClXCX_2 \rightarrow \overline{C\,ClXCX_2C}ClX \qquad (40)$$

The mono-free radicals either add to the chloroethylene or react with each other via combination or disproportionation reactions.

The excited adduct formed in reaction 38c is a species which may undergo many reactions: (1) it may polymerize either with itself or with the parent chloroethylene; (2) it might stabilize as the epoxide; (3) it might react with parent ethylene to give a cyclopropane and a carbonyl compound; (4) it might rearrange to an excited aldehyde which could be stabilized or decompose to free radical products.

A. Individual Substituted Ethylenes

Each of the substituted ethylenes behaves slightly differently from the others, and we now examine them individually.

CCl_2CCl_2. The mercury-sensitized photolysis of N_2O in the presence of C_2Cl_4 at 25 °C yields N_2, CCl_2O, and polymer as exclusive products.[36] The absence of tetrachloroethylene oxide and $c\text{-}C_3Cl_6$ as products indicates respectively that all the $C_2Cl_4O^*$ polymerizes and that none of the CCl_2 adds to C_2Cl_4; reaction 40 is not operative in this system. Since $-\Phi\{C_2Cl_4\} \sim 1$ the polymer does not incorporate additional CCl_2CCl_2, and its formation must come only from reaction 41.

$$CClXCX_2O^* \rightarrow \text{polymer} \qquad (41)$$

The mechanism predicts that

$$\Phi\{CCl_2O\} = k_{38a}/k_{38} \qquad (VII)$$

$$-\Phi\{C_2Cl_4\} = 1 - k_{38a}/2k_{38} \qquad (VIII)$$

$\Phi\{CCl_2O\}$ was found to be 0.19 independent of reaction conditions, so this is the value of k_{38a}/k_{38}. With this value, $-\Phi\{C_2Cl_4\}$ should be 0.9, which is in agreement with the experimental results.

CCl_2CHCl. The products of the reaction were CO, $CHCl_3$, and polymer.[37] The quantum yields of CO and $CHCl_3$ were 0.23 ± 0.01 and 0.14 ± 0.05, respectively. Thus the reaction channels involved in this system are reactions 38b and 38c, with $k_{38b}/k_{38} = 0.23$. Reaction 38b presumably proceeds through an energetic CHClO molecule which rapidly decomposes to HCl + CO. No CCl_2O was produced and the cleavage products gave entirely CCl_2, and no CHCl, diradicals. Most of the HCl and CCl_2 combine to form $CHCl_3$, but some other products must also be formed to account for the difference in the CO and $CHCl_3$ quantum yields.

Presumably $C_2HCl_3O^*$ always polymerizes, since no epoxide or aldehyde was found as products, and the polymerization must proceed without involving additional C_2HCl_3 molecules through reaction 41 since the quantum yield of C_2HCl_3 disappearance was about 1.0.

The mechanism predicts that:

$$\Phi\{CO\} = \Phi\{CHCl_3\} = k_{38b}/k_{38} \qquad (IX)$$

$$-\Phi\{C_2HCl_3\} = 1.0 \qquad (X)$$

The results of the oxidation of $CHClCCl_2$ in the three systems initiated by Cl atoms, Hg 6(^{3}P) and O(^{3}P) are summarized in Table IV. The three systems give consistent findings.

CCl_2CH_2. The reaction of O(^{3}P), prepared from the Hg photosensitization of N_2O, with CCl_2CH_2 was studied at 25 °C.[38] The products of the reaction were CO, $CH_2ClCCl(O)$, polymer, and another unidentified compound. The quantum yields of CO and $CH_2ClCCl(O)$ were 0.35 and 0.06, respectively, independent of reaction conditions.

Twelve possible reaction paths between O(^{3}P) and CCl_2CH_2 were discussed; the final conclusion gave the following mechanism as most likely.[38]

$$\phi = 0.31 \quad O(^3P) + CCl_2CH_2 \rightarrow CO + HCl + CHCl \qquad (38b')$$

$$\phi = 0.55 \quad \rightarrow CCl_2CH_2O^* \qquad (38c)$$

$$\phi = 0.06 \quad \rightarrow CH_2ClCCl(O) \qquad (38d')$$

$$\phi = 0.04 \quad \rightarrow CHCl_2 + HCO \qquad (38e)$$

$$\phi = 0.04 \quad \rightarrow CH_2Cl + CO + Cl \qquad (38e')$$

Reactions 38b′, 38d′, and 38e′ are abnormal in that they involve the migration of a chlorine atom. The first two of these are particularly surprising, since the more usual analog involving hydrogen-atom migration apparently does not occur. The $CCl_2CH_2O^*$ formed in reaction 38c ultimately leads to polymer. Contrary to the situations with CCl_2CCl_2 and $CHClCCl_2$, some additional CH_2CCl_2 is incorporated into the polymer, since $-\Phi\{CH_2CCl_2\}$ exceeds 1.0 and may be as high as 3.0.

cis- and trans-CClHCClH. The Hg-photosensitized decomposition of N_2O in the presence of *cis-* or *trans*-CHClCHCl gives N_2, CO, and polymer as products.[7] HCl was also detected at large conversions. Small amounts of $CH_2ClCCl(O)$ were found, but the quantum yield was ≤0.04. The average values for Φ{CO} were 0.23 and 0.28 for the *cis-* and *trans*-CHClCHCl, respectively. Both isomers gave −Φ{CHClCHCl} up to 5, indicating that the polymer consisted mainly of the chloroethylene.

The reaction goes through three channels:

$$O(^3P) + CHClCHCl \rightarrow CO + HCl + CClH \qquad (38b)$$

$$\rightarrow CHClCHClO^* \qquad (38c)$$

$$\rightarrow CH_2ClCCl(O) \qquad (38d)$$

followed by

$$CHClCHClO^* + CHClCHCl \rightarrow \text{polymer} \qquad (42)$$

$$CClH + CHClCHCl \rightarrow \text{products} \qquad (40')$$

$$2CHCl \rightarrow CHClCHCl \qquad (39)$$

TABLE IV. Oxidation of $CClHCCl_2$

System	Φ{CO}/Φ{CCl_2O}	k_{2b}/k_2
Cl atom	...	0.09
Hg 6(^{3}P)	1.85	0.16
O(^{3}P)	1.7	0.10

The fractional importance of channels 38b and 38d are given by Φ{CO} and Φ{$CH_2ClCCl(O)$}, respectively. Thus $k_{38b}/k_{38} = 0.23$ for the cis isomer and 0.28 for the trans isomer. The ratio $k_{38d}/k_{38} \leq 0.04$.

$CHClCH_2$. The reaction of O(^{3}P) with $CHClCH_2$ gives as products CO, $CH_2ClCH(O)$, $CH_3CCl(O)$, HCl, CH_4, and polymer.[8] The quantum yields depend on the total pressure (mainly N_2O) and are given below for high- and low-pressure conditions.

Product	Φ([N_2O] ≃ 400 Torr)	Φ([N_2O] ≃ 35 Torr)
CO	0.25	0.40
$CH_2ClCH(O)$	0.40	0.25–0.35
$CH_3CCl(O)$	0.09	0.07

The quantum yield of $CHClCH_2$ removal exceeds 1.0, and it as well as Φ{$CH_3CCl(O)$} is independent of total pressure.

The reaction was explained by a scheme similar to that for the reaction of O(^{3}P) with C_2H_4[39] and which is substantially different from that for the other chloro olefins.

$$O(^3P) + C_2H_3Cl \rightarrow C_2H_3ClO^* \qquad (38c)$$

$$C_2H_3ClO^* \rightarrow CH_2 + CO + HCl \qquad (43a)$$

$$\rightarrow CH_2ClCH(O)^* \qquad (43b)$$

$$\rightarrow CH_3CCl(O)^* \qquad (43b')$$

$$CH_2ClCH(O)^* \rightarrow CH_2Cl + HCO \qquad (44)$$

$$CH_2ClCH(O)^* + M \rightarrow CH_2ClCH(O) + M \qquad (45)$$

$$CH_3ClCH(O)^* \rightarrow CH_3 + Cl + CO \qquad (44')$$

$$CH_3CCl(O)^* + M \rightarrow CH_3CCl(O) + M \qquad (45')$$

The excited intermediate, $C_2H_3ClO^*$, can decompose or rearrange to one of the aldehydes which still contain the excess energy of reaction. If not deactivated they decompose to radical fragments. Thus at higher pressure relatively more aldehydes and less CO are produced. The radical fragments react with the C_2H_3Cl to form the polymeric material. Presumably some of the CH_3 radicals abstract a hydrogen atom to give the small amount of CH_4 produced. Reaction 43a has been included for completeness, but in fact there is no evidence that it actually occurs. Apparently the $C_2H_3ClO^*$ is never deactivated to the epoxide, since no epoxide was found.

Slagle et al.[39a] used their technique of crossed molecular beams with photoionization mass spectrometry to examine the reaction of O(^{3}P) with $CHClCH_2$ at 302 K and 1.41 Torr, a pressure very much lower than used by Sanhueza and Heicklen.[8] They found the CH_3 radical channel to proceed with a quantum efficiency of 0.22 and they also found ketene produced with a quantum efficiency of 0.08.

CH_2CH_2. The reaction of O(^{3}P) with C_2H_4 has been interpreted traditionally[39] by the mechanism

$$O(^3P) + CH_2CH_2 \rightarrow CH_2CH_2O^* \qquad (38c')$$

$$CH_2CH_2O^* \rightarrow CH_3CHO^* \qquad (43b'')$$

$$CH_2CH_2O^* + M \rightarrow \overline{CH_2CH_2O} + M \qquad (42'')$$

$$CH_3CHO^* \rightarrow CH_3 + HCO \qquad (44'')$$

$$CH_3CHO^* + M \rightarrow CH_3CHO \qquad (45'')$$

Most of the products could be interpreted as coming from the

TABLE V. Products and Quantum Yields in the Reaction of $O(^3P)$ with Chloro-, Chlorofluoro-, and Fluoroethylenes

Haloethylene	Products[a]	Φ[b]	k_{38a}/k_{38}	k_{38b}/k_{38}	k_{38c}/k_{38}	k_{38d}/k_{38}	k_{38e}/k_{38}	Reference
CCl_2CCl_2	CCl_2O, polymer	0.19	0.19	0	0.81	0	0	Sanhueza and Heicklen[36]
CCl_2CClH	CO, $CHCl_3$, polymer	0.23	0	0.23	0.77	0	0	Sanhueza and Heicklen[37]
CCl_2CH_2	CO, $CH_2ClCCl(O)$, polymer	0.35	0	0.31[c]	0.55	0.06[c]	0.08[d]	Sanhueza and Heicklen[38]
cis-CClHCClH	CO, HCl, polymer	0.23	0	0.23	0.73–0.77	≤0.04	0	Sanhueza and Heidklen[7]
trans-CClHCClH	CO, HCl, polymer	0.28	0	0.28	0.68–0.72	≤0.04	0	Sanhueza and Heicklen[7]
$CClHCH_2$	$CH_2ClCH(O)$, CO, $CH_3CCl(O)$, polymer	~0.4	0	≤0.25	>0.30	0.09 -0.34		Sanhueza and Heicklen[8]
CF_2CF_2	CF_2O, c-C_3F_6	1.0	0.85	0	0.15	0	0	Saunders and Heicklen[46]
CF_2CFCl	CF_2O	1.0						Sanhueza[18]
CFClCFCl	CFClO, polymer	0.80	0.80	0	0.20	0	0	Sanhueza and Heicklen[9]
CF_2CCl_2	CF_2O, $\overline{CCl_2CF_2CCl_2}$	1.0	0	0	1.00	0	0	Sanhueza and Heicklen[9]
CF_2CFH	CF_2O, CHFO							Huie et al.[48]
CF_2CH_2	CO, C_2F_4, CF_2O							Mitchell and Simons[47]
CF_2CHCl	CF_2O, CO, HCl							Mitchell and Simons[47]
CF_2CFBr	CF_2O							Mitchell and Simons[47]
CH_2CHF	CHFO, CH_2O, CO							Huie et al.[48] and Moss[49]
CFHCFH	CHFO							Huie et al.[48]

[a] For more details see text. [b] Quantum yield of the principal oxygenated product (first listed in Products column). $\Phi = k_{38x}/k_{38}$ (where x = a, b, c, or d). [c] These yields are for the abnormal reactions involving Cl atom migration (see text). [d] Total yield = 0.08. About one-half of the yield involves the normal H atom migration; and about one-half of the yield, the abnormal Cl atom migration (see text).

free radical fragments produced in reaction 44″. The yields of both ethylene oxide and CH_3CHO increased slightly with pressure indicating that they were produced, at least in part, from the pressure stabilization of the energetic intermediates. Further evidence for this comes from the work at liquid N_2 temperature where the sole products were ethylene oxide and $CH_3CH(O)$ in a ratio of 1.2.[40]

More recent experiments at room temperature utilizing crossed beams or a fast-flow reactor coupled to a photoionization mass spectrometer[41,42] have confirmed the presence of a small additional process, accounting for 5% of the total reaction, to produce $CH_2CO + H_2$ directly as earlier suggested by Cvetanović.[43,44]

$$O(^3P) + CH_2CH_2 \rightarrow CH_2CO + H_2 \qquad (38f)$$

CH_2CHBr. Slagle et al.[39a,45] have shown that three paths occur in the reaction of $O(^3P) + CH_2CHBr$.

$$O(^3P) + CH_2CHBr \rightarrow CH_3 + BrCO \rightarrow Br + CO \qquad (38a')$$

$$\rightarrow CH_2Br + HCO \qquad (38a'')$$

$$\rightarrow CH_2CO + HBr \qquad (38f')$$

Reactions 38a′ and 38a″ may proceed through energetic intermediate adducts. The relative importance of the three channels was 0.29, 0.51, and 0.20.

CF_2CF_2. Oxygen atoms react with C_2F_4 to produce CF_2O and c-C_3F_6 as exclusive products.[1] The reaction was studied by Saunders and Heicklen[46] at temperatures of 23 and 125 °C over a wide range of oxygen-atom concentrations and with C_2F_4 pressures from 3 to 123 Torr. The quantum yield of CF_2O production is 1.0 for all conditions.

The mechanism of reaction is explained by

$$O(^3P) + CF_2CF_2 \rightarrow CF_2O + CF_2 \qquad (38a)$$

$$\rightarrow C_2F_4O^* \qquad (38c)$$

with channel 38c occurring 15% of the time. The CF_2 and $C_2F_4O^*$ are removed as follows:

$$2CF_2 \rightarrow C_2F_4 \qquad (39')$$

$$CF_2 + C_2F_4 \rightarrow c\text{-}C_3F_6 \qquad (40')$$

$$C_2F_4O^* \rightarrow CF_2O + CF_2 \qquad (41')$$

$$C_2F_4O^* + C_2F_4 \rightarrow CF_2O + c\text{-}C_3F_6 \qquad (42')$$

$C_2F_nH_{4-n}$ (n = 1, 2, and 3). For the fluoroethylenes, there is not a complete study of the reaction mechanism.

Mitchell and Simons[47] studied the reaction of CH_2CF_2 through flash photolysis of NO_2–olefin mixtures and continuous protolysis of NO_2–fluoro olefin mixtures. In the flash photolysis experiment ground-state CF_2 was monitored qualitatively from its uv absorption bands (which persist for >60 ms). Using C_2F_4 as a reference, Mitchell and Simons concluded that CF_2 is produced in large amounts in the CH_2CF_2 reaction when the $[CH_2CF_2]/[NO_2]$ ratio is high (to minimize the competition between NO_2 and CH_2CF_2 for the $O(^3P)$ atom).

The final products from continuous photolysis were CO, C_2F_4, and very small amounts of CF_2O. It was concluded that reaction occurs via

$$O(^3P) + CH_2CF_2 \rightarrow CH_2O + CF_2 \qquad (38a)$$

$$\rightarrow CF_2O + CH_2 \qquad (38a')$$

and that CH_2o was formed with sufficient vibrational energy to dissociate. Since no quantum yields were reported, we can only tentatively outline a mechanism similar to that proposed for the chloroethylenes

$$O(^3P) + CH_2CF_2 \rightarrow CF_2O + CH_2 \qquad (38a')$$

$$\rightarrow CO + H_2 + CF_2 \qquad (38b)$$

$$2CF_2 \rightarrow C_2F_4 \qquad (39')$$

It is interesting to point out that no $\overline{CF_2CH_2CF_2}$ was reported as a product.

For the same olefin both CF_2O and CH_2O were observed as products by Huie et al.[48] However, the authors pointed out that CF_2O could be from a secondary reaction with molecular oxygen in the reaction mixture.

In Table V are the aldehydic products reported by Huie et al.[48] in the reaction of $O(^3P)$ with fluoroethylenes. No quantitative estimates were made.

Moss[49] reported that carbon monoxide is a primary product formed in high yields in the reaction of CH_2CHF with $O(^3P)$. Slagle et al.[39a] have found that at 1.4 Torr pressure, the three reaction channels producing CH_3, CH_2F, and CH_2CO occur with respective quantum efficiencies of <0.07, >0.82, and 0.11.

CFClCFCl. Sanhueza and Heicklen[9] reported on the Hg-photosensitized decomposition of N_2O in the presence of an equilibrium mixture of *cis*- and *trans*-CFClCFCl. The products were N_2, CFClO, polymer, and an unidentified compound.

$\Phi\{CFClO\}$ was ~0.80 independent of a factor of 6.7 change in [CFClCFCl] and a factor of 14 change in I_a (at high N_2O pressures). The values for $-\Phi\{CFClCFCl\}$ showed some scatter, and they varied between 1.0 and 3.4, suggesting that more than one CFClCFCl is removed per $O(^3P)$. The unidentified product was probably c-$(CFCl)_3$, and its relative yield showed no trend with changes in reaction conditions.

The reaction is most easily described by the mechanism:

$$O(^3P) + CFClCFCl \rightarrow CFClO + CFCl \qquad (38a)$$

$$\rightarrow CFClCFClO^* \qquad (38c)$$

$$2CFCl \rightarrow CFClCFCl \qquad (39)$$

$$CFCl + CFClCFCl \rightarrow c\text{-}(CFCl)_3 \qquad (40)$$

$$CFClCFClO^* + CFClCFCl \rightarrow \text{polymer} \qquad (42)$$

with the ratio $k_{38a}/k_{38} = 0.80$.

CF_2CCl_2. The reaction of $O(^3P)$ with CF_2CCl_2 gives CF_2O and 1,1,3,3-tetrachloro-2,2-difluorocyclopropane (c-$CCl_2CF_2CCl_2$), both with quantum yields of about unity and with $-\Phi\{CF_2CCl_2\} = 2$ invariant to reaction conditions.[9] The mechanism consistent with the other chloroolefins was discarded for the following reasons.

(1) No C_2Cl_4 was found.

(2) $\Phi\{c\text{-}CCl_2CF_2CCl_2\}$ should be pressure dependent and intensity dependent unless reaction 39 never occurs.

(3) In the presence of O_2 (discussed in the next section), the long-chain free-radical oxidation should occur and $\Phi\{CF_2ClCCl(O)\}$ should approach 45. In fact, it never reaches 3.0.

(4) In the presence of O_2, the long-chain oxidation should be a function of $[CCF_2CCl_2]/I_a^{1/2}$. In fact, $\Phi\{CF_2ClCCl(O)\}$ is independent of I_a, but dependent on $[CF_2CCl_2]/[O_2]$. Thus, Sanhueza and Heicklen[9] proposed the following mechanism:

$$O(^3P) + CF_2CCl_2 \rightarrow CCl_2CF_2O^* \qquad (38c)$$

$$CCl_2CF_2O^* + CF_2CCl_2 \rightarrow CF_2O + \overline{CCl_2CF_2CCl_2} \qquad (42')$$

This mechanism predicts that

$$\Phi\{CF_2O\} = \Phi\{\overline{CCl_2CF_2CCl_2}\} = 1.0 \qquad (XI)$$

which conformed to the findings.

In the Mitchell and Simons[47] system (discussed above), no CF_2 was produced from CF_2CCl_2 in their flash photolysis experiments, and CCl_2O was the main product from continuous photolysis. Tyerman,[50] who looked for ground-state CF_2 by kinetic spectroscopy after long-wavelength flash photolysis of CF_2CCl_2–NO_2–N_2 mixtures, reported that no CF_2 diradical is released from the reaction.

CF_2CFCl. In the reaction of $O(^3P)$ with CF_2CFCl, Mitchell and Simons[47] reported CF_2O and CFClO as products, the former being the more important. In their experiments with O_2 present, $[CF_2O] \simeq [CFClO]$, so it is possible that the small amount of CFClO detected in the absence of O_2 really came from the reaction with O_2 produced in the reaction of $O(^3P)$ with NO_2.

Preliminary results from our laboratory[18] show that the production of CF_2O has a quantum yield of 1.0, in agreement with Tyerman[50] who reported that no CF_2 was released from the reaction.

B. Mechanism

The results of the various studies are summarized in Table V. Some general comments follow.

(1) There are three types of reactions which are most typified by the three molecules C_2F_4, C_2Cl_4, and C_2H_4. For C_2F_4 the main result of $O(^3P)$ attack is double bond cleavage, reaction 38a; for C_2Cl_4, the principal reaction path is (38c) to form $CCl_2CCl_2O^*$ which then polymerizes all the time; for C_2H_4, the excited intermediate, $CH_2CH_2O^*$, is also formed, but it rearranges to give CH_3CHO or free-radical fragments. There is also some evidence that these products are formed directly via reaction paths 38d and 38e. Mono free radicals or the two-carbon acid halide are never formed with C_2F_4 or C_2Cl_4.

For the fluoroethylenes, $CHFCF_2$, CHFCHF, CH_2CF_2, $CHFCH_2$, CF_2CFCl, and CF_2CFBr, the data are not quantitative. However, no polymer, epoxide, two-carbon carbonyl product, or products expected from mono-free-radicals were found. Consequently, we can assume that the principal reaction path is by carbon–carbon double-bond cleavage, either reaction 38a or 38b.

C_2F_4 and CFClCFCl react with $O(^3P)$ primarily by the double-bond cleavage reaction 38a, but some excited intermediate is produced by channel 38c. CF_2CCl_2 apparently reacts entirely by channel 38c. For C_2F_4 and CF_2CCl_2, the excited intermediate $CX_2CX_2O^*$ always reacts with the parent olefin to give a short-chain polymerization (chain lengths < 10).

With all the chloro olefins the C=C double-bond cleavage paths, reactions 38a and 38b, occur 19–31% of the time. The dominant path is reaction 38c to produce $CClXCX_2O^*$. This molecule leads entirely to polymerization without involving the parent olefin with C_2Cl_4 and $CHClCCl_2$

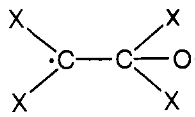
$$CClXCX_2O^* \rightarrow \text{polymer} \qquad (41)$$

$CClXCX_2O^*$ leads almost entirely to polymer for the CH_2CCl_2 and *cis-* and *trans-*CHClCHCl systems, either by reaction 41 or by incorporation of the parent molecule.

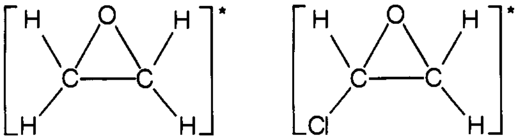
$$CClXCX_2O^* + CClXCX_2 \rightarrow \text{polymer} \qquad (42)$$

$CClXCX_2O^*$ leads primarily to rearrangement for the $CHClCH_2$ and C_2H_4 systems. Thus the two-carbon carbonyl products and the products of mono-free-radical reactions are observed. In C_2H_4 some epoxide is also observed, but this is the only ethylene for which the epoxide was ever reported.

(2) It has been seen that except for C_2H_4, no epoxide has ever been found. Furthermore, except for C_2H_4, CH_2CHBr, $CHClCH_2$, to a minor extent CCl_2CH_2, and *cis-* and *trans-*CHClCHCl, no free-radical or rearrangement products were found. This suggests that with the exception of C_2H_4, CH_2CHBr, and $CHClCH_2$, the excited $CX_2CX_2O^*$ intermediate has a σ-type bond with the oxygen atom localized on one of the carbon atoms, presumably the one at the positive end of the molecule.



Thus this molecule has diradical character (from the spin conservation rules, it should be a triplet) and reacts easily with the parent olefin or with itself. Presumably for C_2H_4 and $CHClCH_2$, the oxygen atom is more centrally located, as has been postulated by Cvetanović.[39]



Thus for these molecules probably the excited intermediates are the triplet states of the corresponding epoxides.

(3) For the unsymmetrical chloroethylenes, the $O(^3P)$ atoms always preferentially attack the less chlorinated carbon atom. The same effect was seen with chlorine atom attack, and the reason must be steric, rather than due to inductive or mesomeric effects.

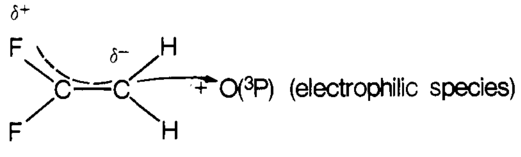
In fluoroethylenes, since two carbonyl products are reported,

TABLE VI. Rate Coefficient for the Reaction of Atomic Oxygen with Haloethylenes at Room Temperature[a]

Olefin	$k/k\{C_2H_4\}$	Source of $O(^3P)$ atom	Reference
CH_2CHF	0.51	Microwave discharge	Huie et al.[48]
	0.38	$N_2O + Hg^*$	Moss[49]
	0.62	Crossed beams	Slagle et al.[39a]
CH_2CF_2	0.43	Microwave discharge	Hue et al.[48]
	0.22	$N_2O + Hg^*$	Moss[49]
cis-CHFCHF	0.32	$N_2O + Hg^*$	Moss[49]
trans-CHFCHF	0.54	$N_2O + Hg^*$	Moss[49]
CHFCHF	0.52	Microwave discharge	Huie et al.[48]
$CHFCF_2$	0.57	$N_2O + Hg^*$	Moss[49]
CF_2CF_2	1.0	$N_2O + Hg^*$	Saunders and Heicklen[46]
	1.0	$NO_2 + h\nu$	Tyerman[50]
	1.6	$N_2O + Hg^*$	Moss[49]
CH_2CHCl	1.0	Microwave discharge	Huie et al.[48]
	0.95	Crossed beams	Slagle et al.[39a]
CH_2CCl_2	1.0	$N_2O + Hg^*$	Sanhueza and Heicklen[38]
cis-CHClCHCl	0.47	$N_2O + Hg^*$	Sanhueza and Heicklen[7]
trans-CHClCHCl	0.11	$N_2O + Hg^*$	Sanhueza and Heicklen[7]
$CHClCCl_2$	0.10	$N_2O + Hg^*$	Sanhueza and Heicklen[37]
CCl_2CCl_2	0.10	$N_2O + Hg^*$	Sanhueza and Heicklen[36]
CF_2CFCl	0.51	$NO_2 + h\nu$	Tyerman[50]
CF_2CCl_2	0.67	$NO_2 + h\nu$	Tyerman[50]
CFClCFCl	0.20	$N_2O + Hg^*$	Sanhueza and Heicklen[9]
CH_2CHBr	0.78	Crossed beams	Slagle et al.[45]
	1.0	Crossed beams	Slagle et al.[39a]
	1.0	Microwave discharge	Huie et al.[48]

[a] $k\{C_2H_4\} = (4.0 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$ at 25 °C.[53-59]

both sides are attacked. However, Mitchell and Simons[47] reported that in CF_2CH_2 the production of CF_2O was very low and that the main product was CO (probably from $CH_2O^* \rightarrow CO$). Maybe, in this case the strong mesomeric effect of the fluorine in the molecule is the explanation.



Moss[49] reported that CO is also produced in large amounts in the reaction of CH_2CHF with $O(^3P)$. In the CF_2CFBr–$O(^3P)$ system the main product was CF_2O[47] in agreement with the idea that steric effects dominate in the addition. Haszeldine and Steele[51] concluded that atom or free-radical attack on CF_2CFCl occurs exclusively at the CF_2 group.

Johari et al.[52] in their paper on addition of CF_3 to chloro olefins concluded that, "If the rate of attack at the $=CF_2$ end of difluoroethylene is assumed to be approximately the same as that for addition to the $=CF_2$ end of chloro-2,2-difluoroethylene, then the rate of attack at a CHCl group is estimated to be 10^3 to 10^4 times slower than attack at the $=CH_2$ group."

C. Rate Coefficient

The rate coefficients for many ethylenes have been measured at room temperature. When the $O(^3P)$ atoms are produced from Hg photosensitization of N_2O, it is most convenient to measure the competition between two olefins for the $O(^3P)$ atom. From the variation in the product yields with relative pressure, the relative rate coefficient can be obtained. If the rate coefficient for one olefin is known, the other can be computed.

Huie et al.[48] measured their rate coefficients using a discharge-flow system coupled to a mass spectrometer by monitoring the decay of the olefin.

In the technique used by Tyerman,[50] ground-state CF_2 was monitored by kinetic spectroscopy after the long-wavelength photolysis of NO_2 (to produce $O(^3P)$) in the presence of C_2F_4 and a competitive olefin diluted in N_2. The CF_2 was produced in the $O(^3P)$–C_2F_4 reaction, and its diminution in the competitive system gave a measure of the relative rate coefficient.

The results of the different studies are listed in Table VI. Rates relative to C_2H_4 are reported. For C_2H_4 the room-temperature rate coefficient is $(4.0 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$.[42,53-59a] The rate coefficients for C_2H_4, C_2F_4, CH_2CHCl, and CH_2CCl_2 are equal to each other and greater than the rate coefficients for the other substituted ethylenes. The partially fluorinated ethylenes have rate coefficient one-third to two-thirds that of C_2H_4. The presence of chlorine on both carbon atoms (except for *cis*-CHClCHCl) drops the rate to about 0.1 that for C_2H_4.

Moss[49] pointed out that, "In considering the reactivities of atoms or free radicals, it is usual to seek correlation with observed or calculated properties of the reactant molecules. Successful correlation often provides useful indication of the nature of the radical reactants and the main factor controlling reactivity. The rates of reaction of $O(^3P)$ with hydrocarbon olefin correlates well with excitation energies and ionization potential of the olefin.[39] Since these properties show the ease with which an electron may be removed or promoted from the π orbital of the ground-state molecule, *electrophilic behavior of $O(^3P)$ is indicated.*" These observations, and others, have led Cvetanović to suggest that the transition state for the reaction is a π complex with the oxygen atom placed approximately centrally between the carbon atoms forming the double bond.

Moss[49] measured the relative rate constant for the reaction of oxygen atoms with the fluorinated ethylenes. The results (in Table VI) were compared with data for the other atoms and radicals with the same olefins and briefly discussed in terms of the electronic changes produced in the double bond by fluorine substitution. The $O(^3P)$ reactivities showed no correlation with the ionization potential.

The reactivities of the chlorinated ethylenes show a correlation between the reactivities with $O(^3P)$ and the ionization potentials. The rate of reaction decreases (more chlorinated) as the ionization potential decreases. However, this correlation is in the opposite direction of that if $O(^3P)$ is an electrophilic species. The results for oxygen atoms are compared in Table VII with results for other atoms and radicals adding to chloro- and chlorofluoroethylenes. Always C_2Cl_4 is the least reactive, and in a general way the inclusion of chlorine in the olefinic molecule decreases the rate.

cis-CClHCClH reacts faster than the trans isomer in the $O(^3P)$ reaction. The significant difference for the rate coefficients for the two isomers presumably reflects steric factor differences.

It is interesting to note that, for the reaction of $O(^3P)$ with CHFCHF and C_4H_8-2, the rate coefficient is also larger for the trans compounds than for the cis compounds by respective factors of 1.7[49] and 1.6.[60] However, the reactions of CH_3O listed in Table VII show that the cis isomer reacts faster with CH_3O than does the trans isomer.

V. Reaction with $O(^3P)$ in the Presence of O_2

The oxidation of the halogenated ethylenes by $O(^3P)$ atoms in the presence of O_2 may proceed by three different routes:

(1) A chain mechanism initiated by the oxidation of the substituted methylene, CX_2. This process is important for C_2Cl_4, $CHClCCl_2$, CH_2CCl_2, *cis*- and *trans*-CHClCHCl, CFClCFCl, and C_2F_4.

(2) The oxidation of the $CX_2CX_2O^*$ intermediate. This process is important for C_2F_4, CF_2CCl_2, and $CHClCH_2$.

(3) The oxidation of the mono-free-radical fragments, a process of importance in C_2H_4 and $CHClCH_2$.

A. Methylene Oxidation

Dependent on the parent ethylene, the $O(^3P)$ atom can react with it to produce any of the following methylenes: CCl_2, CH_2, CF_2, CClH, CClF, or CFH. The spin conservation rules predict that these methylenes will be produced in their triplet states and thus be reactive with O_2. This is to be contrasted for the singlet carbene species, which have been shown to be unreactive with O_2 at room temperature for CH_2,[64] CCl_2[65] CFCl,[65] and CF_2[1] (singlet CF_2 reacts with O_2 at elevated temperatures to give $CF_2O + O(^3P)$).

All the evidence suggests that when CX_2 species are produced in the $O(^3P)$–CX_2CX_2 reaction, they are produced exclusively in the triplet state. However, the triplet methylenes react with O_2 by three different routes depending on the methylene involved. (1) The triplet species CCl_2,[36,37] CClH,[7] and CClF[9] react with O_2 as follows

$$^3CClX + O_2 \rightarrow XO + ClCO \tag{46}$$

and the ClCO species can readily fall apart.

$$ClCO \rightarrow Cl + CO$$

(2) The triplet CF_2 adds to O_2.[1]

$$^3CF_2 + O_2 \rightarrow CF_2O_2 \tag{24}$$

(3) The triplet CH_2 gives[43]

$$^3CH_2 + O_2 \rightarrow HCOOH \tag{47a}$$

$$\rightarrow H_2O + CO \tag{47b}$$

Thus in the first case mono free radicals are produced; in the second case, diradicals; and in the third case, stable products. The detailed fate of triplet CFH with O_2 is unknown, but Gordon and Lin[66] observed HF laser emission from the reaction of CHF with O_2. They attributed this product to the formation of excited FCOOH which decomposes to give $HF^{\pm} + CO_2$. Thus, at least part of the time, CHF oxidizes analogously to CH_2 to give molecular products directly.

The difference in the three reactions is probably energetics. In all likelihood in all three cases the adduct CX_2O_2 is formed first. With CF_2O_2, any rearrangement is endothermic and does not occur. For the other species presumably they rearrange to XC(O)OX, which decomposes to XO + XCO. Only in the case of HC(O)OH does stabilization occur. However, the HC(O)OH initially formed on rearrangement contains excess energy, and apparently this energy is sufficient for reaction 47b to proceed if the molecule is not deenergized.

B. Oxidation of $CX_2CX_2O^*$

The reaction of $CX_2CX_2O^*$ with O_2 can proceed in two ways. The route which prevails with $CF_2CF_2O^*$ is:

$$O_2 + CF_2CF_2O^* \rightarrow CF_2O_2 + CF_2O$$

On the other hand, with $CCl_2CF_2O^*$, the process is

$$O_2 + CCl_2CF_2O^* \rightarrow CF_2O + ClCO + ClO$$

$CHClCH_2O^*$ apparently can react by either route to produce the diradical or monoradical products, respectively. For the other ethylenes, the oxidation of $CHClCH_2O^*$ has not been elucidated, since it appears to be an unimportant process.

TABLE VII. Relative Reactivities of Chloro- and Chlorofluoroethylenes with Atoms and Radicals in the Gas Phase at Room Temperature[a]

Ethylene	$O(^3P)$[b]	CCl_3[c]	CH_3O[d]	Cl[e]	Hg $6(^3P)$	IP, eV[f]
			Chloroethylenes			
CCl_2CCl_2	0.10	<0.003	0.18	0.30[g]	1.7[h]	9.34
CCl_2CHCl	0.10	0.16	0.40	0.79	2.3[i]	9.48
CCl_2CH_2	1.0			0.72		9.83
cis-CClHCClH	0.11	0.05	1.28	1.37		9.65
trans-CClHCClH	0.47		0.95	0.90		9.64
$CClHCH_2$	1.0	1.0[j]		1.0[j]		10.00
CH_2CH_2	1.0[j]		1.0[j]		1.0[j]	10.66
			Chlorofluoroethylenes			
CF_2CF_2	1.0		2.22		0.20[k]	10.11
CF_2CFCl	0.51					9.84
CF_2CCl_2	0.67	0.06				9.65
CFClCFCl	0.20					

[a] A very complete table is given by Moss[49] for the fluoroethylenes. [b] For references, see Table V. [c] Reference 52 at 150 °C. [d] Reference 61. [e] Reference 63. [f] Reference 62. [g] Reference 23. [h] References 27 and 29. [i] Reference 29. [j] Relative reactivity set at 1.0. [k] References 1 and 29.

C. Individual Molecules

C_2Cl_4. A long-chain process is involved which produces the same products as in the chlorine-atom-initiated reaction, and the ratio of CCl_3CClO produced to CCl_2O produced is 2.0 at 25 °C,[36] similar to the ratio of 2.5 found in the chlorine atom system. However, the rate law is different, the quantum yield of chlorinated product formation being proportional to $[C_2Cl_4]/I_a^{1/2}$. In addition CO is formed with a quantum yield of 0.18, independent of conditions. This value is identical with the CCl_2O yield in the $O(^3P)$–C_2Cl_4 system in the absence of O_2.

$CHClCCl_2$. For $CHClCCl_2$ the free-radical long-chain oxidation is observed, as in the case of C_2Cl_4.[37] The chain lengths increase with $[CHClCCl_2]/I_a^{1/2}$, but at less than a linear rate.

CHClCHCl. Again the free-radical long-chain oxidation is observed.[7] However, the chain length is almost independent of $[CHClCHCl]/I_a^{1/2}$ for the trans compound and only slightly dependent on this parameter for the cis compound. Geometrical isomerization is also observed.

CH_2CCl_2. The free-radical long-chain process occurs, and the chain lengths increase with $[CH_2CCl_2]/I_a^{1/2}$, but less than proportionately.[38] Thus the rate law is similar to that for $CHClCCl_2$. The CO quantum yield increases from 0.35 in the absence of O_2 to 0.78 ± 0.16 in the presence of O_2, independent of reaction conditions.

CFClCFCl. As with $CHClCCl_2$ and CH_2CCl_2, this molecule exhibits the free-radical long-chain oxidation which increases less than proportionately with $[CFClCFCl]/I_a^{1/2}$.[9] The quantum yield of oxidation reaches an upper limiting value of 140. CO was also produced with a quantum yield of 0.80, exactly equal to the CFClO yield in the $O(^3P)$–CFClCFCl system in the absence of O_2.

CF_2CCl_2. In this system a short-chain process was observed which did not depend on $[CF_2CCl_2]/I_a^{1/2}$, but rather on $[CF_2CCl_2]/[O_2]$. $\Phi\{CF_2O\}$ was equal to 1.0 invariant to the reaction parameters.[9] These results were interpreted by a mechanism analogous to that found for C_2F_4[1]:

$$CCl_2CF_2O^* + CF_2CCl_2 \rightarrow CF_2O + \overline{\mathrm{C}Cl_2CF_2\mathrm{C}}Cl_2 \tag{48}$$

$$CCl_2CF_2O^* + O_2 \rightarrow CF_2O + ClO + ClCO \tag{49}$$

Reaction 49 becomes the initiating step for the chain reaction,

TABLE VIII. Reaction of Chloroethylenes with $O(^3P)$ in the Presence of O_2

Olefin	$[Olefin]/I_a^{1/2}$, $(Torr\ s)^{1/2}$	$[Olefin]/I_a^{1/2}$ dependence	$\Phi\{CO\}$	$\Phi\{OX\}_\infty$	$\Phi\{OX\}_\infty/\Phi\{OX\}_{Cl}$ [a]	$(k_{38a}+k_{38b})/k_{38}$ [b]	Reference
CCl_2CCl_2	9.9–175	Linear	0.18	*c*		0.19	Sanhueza and Heicklen[36]
CCl_2CHCl	48–1150	Less than linear	*d*	77.0	0.38	0.23	Sanhueza and Heicklen[37]
CCl_2CH_2	94–2000	Less than linear	0.78[e]	55.0	0.32	0.35	Sanhueza and Heicklen[38]
cis-CHClCHCl	36.5–687	Almost none	*d*	7.0	0.32	0.23	Sanhueza and Heicklen[7]
trans-CHClCHCl	32.5–638	Almost none	*d*	7.0	0.32	0.28	Sanhueza and Heicklen[7]
CFClCFCl	40.5–684	Less than linear	0.80	160	0.76 (0.38 × 2)	0.80	Sanhueza and Heicklen[9]

[a] $\Phi\{OX\}_{Cl}$ from Table I. [b] Values obtained when O_2 was absent (Table V). [c] Was never reached under the actual experimental condition. [d] CO was also produced in the chain. [e] $\Phi\{CO\} = 0.35$ in the absence of O_2.

and the mechanism predicts $\Phi\{CF_2ClCCl(O)\}/\Phi\{CO\}$ in this system should equal $\Phi\{CF_2ClCCl(O)\}$ in the chlorine-atom initiated oxidation at high pressures. The former quantity varies between 28 and 45, and the latter quantity is about 45, so that the agreement is not too bad.

Reactions 48 and 49 must be simplifications of a much more complex process since they predict $\Phi\{CO\} = 1.0$ and $\Phi\{c\text{-}CCl_2CF_2CCl_2\} = 0$ at low values of $[CF_2CCl_2]/[O_2]$, and $\Phi\{CO\} = 0$ and $\Phi\{c\text{-}CCl_2CF_2CCl_2\} = 1.0$ at high values of $[CF_2CCl_2]/[O_2]$, contrary to the observations. Possibly $CCl_2CF_2O^*$ represents several isomeric species, one of which always goes by reaction 48, one of which always goes by reaction 49, and one or more which can proceed by either route.

C_2F_4. The reaction of oxygen atoms with C_2F_4 in the presence of O_2 was studied briefly by Saunders and Heicklen[46] at room temperature and in more detail at 23 and 125 °C by Heicklen and Knight.[67] In addition to CF_2O and $c\text{-}C_3F_6$ (found in the absence of O_2), the products included tetrafluoroethylene oxide. The results were reviewed and discussed elsewhere.[1] The results were explained by a biradical mechanism which for the methylene is

$$^3CF_2 + O_2 \rightarrow CF_2O_2 \tag{24}$$

$$CF_2O_2 + C_2F_4 \rightarrow 2CF_2O + {}^3CF_2 \tag{23a}$$

$$\rightarrow CF_2O + CF_2CF_2\overset{|}{O} \tag{23b}$$

$$2CF_2O_2 \rightarrow 2CF_2O + O_2 \tag{50}$$

and for the excited molecule mechanism is

$$C_2F_4O^* + C_2F_4 \rightarrow c\text{-}C_3F_6 + CF_2O \tag{42'}$$

$$C_2F_4O^* + O_2 \rightarrow CF_2O + CF_2O_2 \tag{51}$$

$CHClCH_2$. Vinyl chloride is unique among the chloro olefins and does not oxidize like any of the higher homologs. Its oxidation follows more nearly the pattern of C_2F_4 except that there is no chain in the $O(^3P)$–O_2–$CHClCH_2$ system; the products are CHClO, CO, HCl, and HCOOH.[8]

Also a very surprising result occurs; namely no C_2 carbonyl compounds are produced. The O_2 must intercept the intermediate in a scheme such as

$$C_2H_3ClO^* + O_2 \rightarrow CHClO^* + CH_2O_2 \tag{51a'}$$

$$\rightarrow HCl + CO + CH_2O_2 \tag{51b'}$$

The CH_2O_2 can either rearrange to HCOOH or decompose to CO + H_2O

$$CH_2O_2 \rightarrow HCOOH \tag{52a}$$

$$\rightarrow CO + H_2O \tag{52b}$$

From the data it was difficult to assess the relative importance of the products observed. However, a reasonable designation for the initial quantum yields was $\Phi\{CO\} \sim 0.6$, $\Phi\{HCOOH\} \sim 0.85$, and $\Phi\{CHClO\} \sim 0.6$. With this assessment, $k_{51a'}/k_{51'} \sim 0.6$ and $k_{52a}/k_{52} \sim 0.8$.

D. Rate Law

There are two general rate laws:

(1) The diradical mechanism which involves the oxidation of CX_2 and $CX_2CX_2O^*$. If there is a chain (C_2F_4, CF_2CCl_2) the chain lengths are dependent on the ratio $[CX_2CX_2]/[O_2]$. The rate law has been discussed in detail in C_2F_4 elsewhere.[1]

(2) The monoradical chain mechanism which applies to all the chloro olefins studied, except CF_2CCl_2 and $CHClCH_2$. The chain lengths depend on the parameter $[CClXCX_2]/I_a^{1/2}$ when the $O(^3P)$ atom is generated in steady-state photolysis. Since the rate of the chain propagation step is proportional to $[CClXCX_2]$, termination by a radical–radical mechanism is suggested in which one radical is the chain carrier (i.e., Cl atoms) and the other radical must be one that is absent in the chlorine-atom initiated or Hg-photosensitized oxidations, since in those systems there is no intensity dependence. The indicated reactions are

$$Cl + XCO \rightarrow ClX + CO \tag{53}$$

$$ClO + ClCO \rightarrow Cl_2O + CO \tag{54a}$$

$$\rightarrow Cl_2 + CO_2 \tag{54b}$$

The initiating reactions are:

$$^3CCl_2 + O_2 \rightarrow ClO + ClCO \tag{46'}$$

$$^3CClH + O_2 \rightarrow HO + ClCO \tag{46''}$$

$$^3CClF + O_2 \rightarrow FO + ClCO \tag{46'''}$$

and the ClCO can decompose via

$$ClCO \rightarrow Cl + CO$$

The ClO and HO radicals react rapidly with the olefins to initiate the chain. However, the FO radical is apparently a terminating radical, since in the CFClCFCl system, the chain length was only one-half that expected if FO propagated the chain.

If the termination is principally by reactions 53 and 54, which is the case at low values of $[CClXCX_2]/I_a^{1/2}$, then the oxidation chain length will be proportional to $[CClXCX_2]/I_a^{1/2}$. On the other hand, at high values of $[CClXCX_2]/I_a^{1/2}$, termination is principally by reactions 4b and 4b′. The chain length should be independent of the reaction parameters, and should be equal to that in the chlorine-atom initiated system multiplied by the yield of CXCl radicals produced in the primary step when $O(^3P)$ reacts with $CClXCX_2$ (one-half that value for CFClCFCl, since FO is not a propagating radical). Thus

$$\Phi\{OX\}_\infty/\Phi\{OX\}_{Cl} = (k_{38a} + k_{38b})/k_{38} \tag{XII}$$

where $\Phi\{OX\}_\infty$ is the upper limiting oxidation quantum yield at high $[CClXCX_2]/I_a^{1/2}$ in the $O(^3P)$–O_2–$CClXCX_2$ system, and $\Phi\{OX\}_{Cl}$ is the oxidation yield in the chlorine-atom-initiated oxidation. The right-hand side of eq XII also can be obtained independently from the $O(^3P)$–$CClXCX_2$ system in the absence of O_2. Thus eq XII relates, in one expression, the principal features of the chlorine-atom-initiated oxidation, the $O(^3P)$ oxidation, and $O(^3P)$–O_2–CX_2ClCX_2 oxidation.

Table VIII summarizes the results obtained for the upper limit long-chain oxidation in the O(^{3}P)–O_2–CClXCX$_2$ system. The values of $\Phi\{OX\}_\infty/\Phi\{OX\}_{Cl}$ agree quite well with the values of (k_{38a} + k_{38b})/k_{38} obtained in the absence of O_2.

VI. Reactions with Ozone

Surprisingly, in spite of their commercial importance and possible biological significance of some of the haloethylenes, relatively limited kinetic studies have been carried out on the ozonolysis reactions of these compounds. The earliest work appears to be as recent as 1966,[68] and, apparently, subsequent studies have originated only from Cvetanović and coworkers at the Canadian National Research Council,[69] from the group in Milan,[91,111–113] and from our laboratory.[5,70,71] The first group reported on the kinetics of ozonolysis of various chloroethylenes in CCl_4 solution while our investigations have dealt with the gas-phase and the low-temperature solid-phase reactions of several of the same chloroethylenes. Although some of our studies have not yet been published, the important conclusions resulting from them will be reviewed here. Also, for the sake of completeness, the ozonolysis data on ethylene itself will be included in this review.

A. Review of the Experimental Data

C_2H_4. The reaction of ethylene with ozone has been studied in the vapor phase under chemiluminescent conditions by Finlayson et al.[72,73] and under nonchemiluminescent conditions by several research groups.[74–83,107–110] Experimental data for the liquid phase reaction originate from the laboratories of Cvetanović[69,84] and of Kuczkowski.[85–88] We have reported previously on the reaction carried out in the solid phase at low temperatures[88] and on the vapor-phase decomposition of one of the relatively stable reaction products obtained from the liquid- and solid-phase reactions.[89]

In their study of the chemiluminescent reaction, Finlayson et al.[72,73] employed a flow system in which excess olefin reacted with ozone (about 2 mol % diluted in O_2, N_2, or He). The total pressures were 2–10 Torr. Emission was seen from vibration–rotation bands of HO with $v \leq 9$. The emission was virtually identical with the Meinel bands seen from the reaction of H with O_3

$$H + O_3 \rightarrow O_2 + HO^\ddagger \qquad (v \leq 9) \qquad (55)$$

thus confirming that H atoms are produced under the experimental conditions used. The emission yield was $\sim 10^{-7}$ for the 9 → 3 transition per molecule of reactant consumed at 4.6 Torr total pressure. Also seen was emission from electronically excited CH_2O ($^1A'' \rightarrow {}^1A_1$) and OH ($A^2\Sigma \rightarrow X^2\Pi$), the yield of the former emission being $\sim 10^{-7}$ per molecule of reactant consumed. The electronically excited HO emission was seen only in N_2-buffered mixtures, but the other two emissions were seen in either N_2 or O_2 buffered mixtures. With the assumption of 1:1 reactant stoichiometry, the rate coefficient was found to be five times larger in N_2 than in O_2 at 2–10 Torr total pressure and reactant fractions of $O_3 \sim 50$ ppm and $C_2H_4 \sim 400$ ppm. In O_2 the rate coefficient at room temperature was $(1 \pm 1) \times 10^3$ M^{-1} s^{-1}.

Cadle and Schadt[74] appear to have been the first to study quantitatively the kinetics of the ethylene–ozone reaction. Infrared spectroscopy was used to follow the decay of ozone, and the reactant pressures were in the range of 0.1 to 3 Torr. The consumption ratio $[C_2H_4]/[O_3]$ was reported to vary between 1.9 and 3.2 and the products were not identified. The initial rates, which were first order in each reactant, gave a second-order rate constant of 2.1×10^3 M^{-1} s^{-1}. Evidently, the rate showed no dependence on oxygen pressure (150 to 650 Torr) or on temperature (30 to 50 °C). Unidentified transitory products were reported at room temperature by Heath et al.[108] using a long-path infrared cell for analysis, but these results have never been confirmed.

The second-order kinetics was subsequently confirmed by Hanst et al.,[75] Bufalini and Altshuller,[79] DeMore,[80] and others.[82,83,109,110] Bufalini and Altshuller[79] used in their work a 12-l. static reactor kept at 25 °C and under a dynamic condition, variable volume vessel (0.5 to 12 l.) with temperature kept between 30 and 100 °C. Reactant concentrations were in the parts per million range, and air was used as diluent. Ethylene was analyzed by gas chromatography while the iodide titration method was used for ozone. Complete stoichiometry was not reported, but the consumption ratio $[C_2H_4]/[O_3]$ was found to be near unity at low ethylene concentrations and to increase to a limiting value of about 1.6 as the olefin pressure was increased. Bufalini and Altshuller reported the experimental Arrhenius frequency factor and activation energy to be 1.7×10^6 M^{-1} s^{-1} and 4.2 ± 0.4 kcal/mol, respectively. At 25 °C, the latter parameters correspond to a rate constant of 1.6×10^3 M^{-1} s^{-1}.

Similar Arrhenius parameters were reported by DeMore[80] although his reaction temperatures were in the range from −40 to −95 °C. The rates in this temperature range were still independent of the presence of oxygen, and the consumption ratio $[C_2H_4]/[O_3]$ was 1.0 ± 0.3 in the absence of O_2 and 1.2 ± 0.3 with O_2. DeMore also observed aerosol formation which was reduced by not using any diluent gas. However, infrared analysis apparently provided no information concerning the nature of this aerosol or of any other reaction products.

More recently Stedman et al.[82] and Herron and Huie[83] have examined the ozonolysis of ethylene at low reactant pressures. In the work of Stedman et al., the reactant concentrations were in the parts per million range and the total pressures were kept at 1 atm. Only a single temperature of 26 ± 2 °C was used in this work, and the second-order rate constant was found to be 0.93×10^3 M^{-1} s^{-1} in either O_2 or N_2 diluent. Herron and Huie followed the reaction by mass spectroscopy in the temperature range of −40 to 90 °C. Ethylene pressures were below 1 Torr but kept about ten times greater than the ozone pressures. These authors observed with argon carrier gas that nonreproducible results were obtained and the apparent second-order rate constants were much greater than those obtained with O_2 buffer gas. With oxygen at about 3 Torr, the resulting second-order rate constants and their Arrhenius parameters were in close agreement with values obtained by other investigators.

The most recent reports of rate parameters are by Japar et al.[109] and Becker et al.[110] Japar et al.[109] studied the reaction at room temperature with initial O_3 concentrations 1–10% of the olefin concentrations. The O_3 concentrations were monitored with the NO–O_3 chemiluminescence technique, and the rate coefficient was found to be 1.1×10^3 M^{-1} s^{-1}. Becker et al.[110] studied the reaction at a total pressure of 6–800 mTorr between 280 and 360 K. The rate coefficient in both the absence and presence of O_2 fitted the expression $7.2 \times 10^6 \exp\{(-4950 \pm 200)/RT\}$ M^{-1} s^{-1} which gives a value of 1.7×10^3 M^{-1} s^{-1} at 25 °C.

The difference in rate coefficient and mechanism in the presence of O_2 found by Herron and Huie[83] and Finlayson et al.[73] confirmed the earlier report of Wei and Cvetanović[78] who found that the ratio of olefin to ozone consumed is unity in the absence of O_2 but between 1.4 and 2.0 in its presence. Furthermore the relative rate coefficient (compared to the i-C_4H_8–O_3 reaction) was different in the O_2 and N_2 buffered systems.[78]

Herron and Huie[83] also studied the ozonolysis of propylene and found that its apparent second-order rate constant decreased by a factor of almost 2 as the O_2 pressure was increased to about 1 Torr. At higher O_2 buffer gas pressures, the second-order rate constants remained constant and at a value of 6.36×10^3 M^{-1} s^{-1} (25 °C) which agreed with those reported by earlier workers.

TABLE IX. Kinetics of Ethylene–Ozone Reaction in the Presence of Excess O_2

Investigators	Species followed[a]	Temp, °C	Reactants Torr	$[C_2H_4]/[O_3]$ consumption	Arrhenius parameters: E, kcal/mol	Arrhenius parameters: A, M^{-1} s^{-}	k at 25 °C, M^{-1} s^{-1}
Cadle and Schadt[74]	O_3 (IR)	30 to 50	0.1 to 3	2 to 3	0	2.1×10^3	2.1×10^3
Bufalini and Altshuler[79]	O_3 (KI) C_2H_4 (GC)	30 to 100	Ppm range	1 to 1.6	4.2 ± 0.4	1.7×10^6	1.6×10^3
DeMore[80]	O_3 (UV)	−95 to −40	2 to 20	1.0 ± 0.3 1.2 ± 0.3(O_2)	4.7 ± 0.2	2.0×10^6	0.79×10^3
Stedman et al.[82]	O_3 (NO) C_2H_4 (GC)	26	Ppm range				0.93×10^3
Herron and Huie[83]	O_3 (MS)	−40 to 90	Ppm to 1		5.1 ± 0.3	5.4×10^6	1.02×10^3
Finlayson et al.[73]	O_3 (UV)	25	$\sim 0.5 \times 10^{-3}$(O_3) $\sim 4 \times 10^{-3}$(C_2H_4)				1.0×10^3
Becker et al.[110]	O_3 (NO)	7 to 87	$(6 \text{ to } 800) \times 10^{-3}$		5.0 ± 0.2	7.2×10^6	1.7×10^3

[a] IR = infrared spectroscopy. KI = KI titration. GC = gas chromatography. UV = ultraviolet spectroscopy. NO = nitric oxide chemiluminescence. MS = mass spectroscopy.

TABLE X. Infrared Spectra of Primary and Secondary Ethylene Ozonide[a]

Secondary ozonide: Vapor (30 °C)	Secondary ozonide: Solid (−190 °C)	Primary ozonide Solid (−190 °C)	Tentative assignment
2996 w	3050 w		CH_2 stretch
2974 s	2980 m		CH_2 stretch
2900 s	2910 s		CH_2 stretch
	2894 m		CH_2 stretch
	1646 w		combination
	~1480 w		CH_2 deformation
~1380 w	1395 vw		CH_2 deformation
		1390 w	CH_2 deformation
~1350 w	1350 m		CH_2 twist
		1325 w	CH_2 twist
1260 w			Difference band
		1214 w	CC stretch
~1207 w	1212 m		CO stretch
1133 m	1130 m		CH_2 wag
		1125 w	CH_2 wag
1082 vs	1060 vs		CO stretch
~1038 m	1020 s		CO stretch
		983 m	OO stretch
957 vs	932 vs		CO stretch
		927 m	CO stretch
~933 m	917 m		OO stretch
		843 w	OO stretch
798 m	804 s		Ring bend
	733 w		Ring bend
		730 m	Ring bend
698 w	696 m		CH_2 rock
		687 w	CH_2 rock
		650 m	Ring bend
		410 w	Ring bend
~400 w	405 w		Ring bend

[a] Frequencies are in cm^{-1} unit.

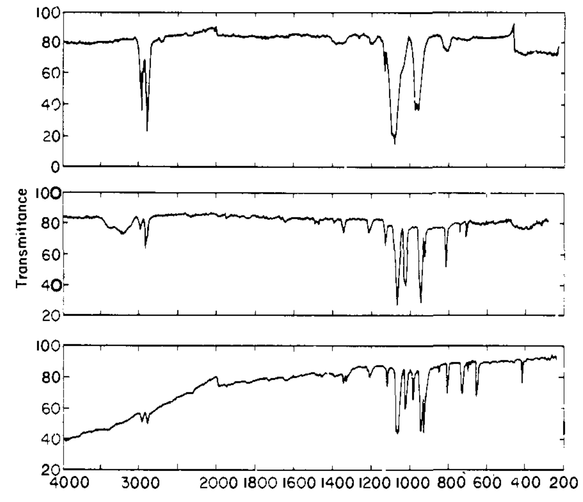


Figure 4. Infrared spectra of primary and secondary ethylene ozonides at liquid nitrogen temperature. In part from Hull et al.[88]

A summary of the kinetic data for the ozonolysis of ethylene is presented in Table IX. Experimental results obtained by Cvetanović and coworkers[76-78] are not included here since only relative rates of ethylene with respect to other olefins were obtained. However, on the basis of analysis by gas–liquid chromatography, Vrbaski and Cvetanović[77] found that 1 mol each of C_2H_4 and O_3 gave 0.25 mol of HCOOH, 0.019 mol of CH_3CHO, and small amounts of other unknown products.

The only attempt of a quantitative kinetic study of the ethylene–ozone reaction in the liquid phase was that by Williamson and Cvetanović.[84] Carbon tetrachloride solution was used by these investigators, but because of loss of olefin from the solution the kinetic results were inconclusive. However, by assuming that the relative rates with respect to 1-hexene were the same in the vapor and CCl_4 solution, Williamson and Cvetanović[69] estimated the second-order rate constant for the ethylene–ozone reaction in CCl_4 solution at 25 °C to be about 2.4×10^4 M^{-1} s^{-1}.

Other liquid-phase studies reported in the literature appear to deal primarily with product identification for mechanistic purposes. Inert solvents and reduced temperatures have been used in these studies in order to minimize the decomposition of the reaction intermediates or products. Under these experimental conditions, some higher molecular weight peroxides are obtained, but the major reaction product is the 1,2,4-trioxacyclopentane (commonly called secondary ethylene ozonide or simply ethylene ozonide). The infrared spectra of ethylene ozonide in the vapor phase at 30 °C and in the solid phase at liquid nitrogen temperature are shown in Figure 4. Our vapor-phase spectrum is essentially the same as that reported first by Garvin and Schubert.[90] Band frequencies and their tentative assignments are given in Table X. The complete microwave structure of ethylene ozonide has been determined by Gillies and Kuczkowski.[85,86] The molecule has a half-chair conformation (C_2 point group) with the geometry as shown in Figure 5, but no evidence of free or hindered ring pseudo-rotation was found. This ozonide also has a dipole moment of 1.09 D, and on the basis of temperature dependence of its microwave line intensities a low-frequency fundamental at 200 ± 40 cm^{-1} was predicted by Gillies and Kuczkowski as a possible ring bending vibrational mode. These investigators also carried out the low-temperature liquid-phase ozonolysis reaction in the presence of formaldehyde-^{18}O and showed that the oxygen isotope appears exclusively in the epoxy position of the ozonide.[85-87] In addition, when ethylene-d_1 was used in the reaction, ethylene-d_0 ozonide and two -d_1 species, all in about equal amounts, and smaller quantities of three types of d_2 species were identified by microwave spectroscopy. Above room temperature, gaseous ethylene ozonide decomposes slowly by a first-order process giving quantitatively formaldehyde and formic acid as products.[89] The first-order rate constant has been determined in the temperature range of 46 to 85 °C to be $k\,(\mathrm{s}^{-1}) = 10^{13.60}\exp(-27.5\ \mathrm{kcal\ mol}^{-1}/RT)$.[89]

The reaction of ethylene with ozone in the solid phase has been studied by Hull et al.[88] with infrared spectroscopy. As the reactants were warmed from liquid nitrogen temperature to about −170 °C, a new set of infrared absorption bands appeared indicating the formation of one major primary product. On further warming to temperatures near −100 °C, this primary product decayed into the known secondary ethylene ozonide. Vaporization of the reaction mixture and its spectroscopic analysis showed that the secondary ethylene ozonide was the final major product with formaldehyde and formic acid being minor products. Also, small amounts of polymeric material remained on the low-temperature infrared window. From the frequencies of the absorption bands of the primary product and from the fact that similar sets of bands were displayed by the initial products in reactions of other olefins with ozone, the primary species of the ethylene–ozone solid-state reaction at low temperatures was identified as the 1,2,3-trioxacyclopentane (primary ethylene ozonide). The infrared spectrum of a solid sample containing both the primary and the secondary ethylene ozonide is shown in Figure 4. Frequencies of the primary ozonide bands are listed in Table X. The most characteristic band in the spectrum of this ozonide at liquid nitrogen temperature is the intense sharp band at 983 cm^{-1} which does not overlap with bands of other species present in the reaction mixture.

C_2F_4. According to Heicklen[68] and later confirmed by Gozzo and Camaggi,[91] only carbonyl fluoride and oxygen are observed as products of the vapor-phase ozonolysis of tetrafluoroethylene at room temperature. Two moles of carbonyl fluoride was obtained from each mole of olefin, so the reaction stoichiometry is evidently

$$2\mathrm{C_2F_4} + 2\mathrm{O_3} \rightarrow 4\mathrm{CF_2O} + \mathrm{O_2} \qquad (56)$$

The kinetics of reaction 56 at 25 °C was studied by Heicklen for ozone and olefin pressures in the range of 0.7–15 Torr and 0.2–6 Torr, respectively. Initial rates, $R_i\{\mathrm{CF_2O}\}$, were determined by following the infrared carbonyl band of $\mathrm{CF_2O}$. At constant $\mathrm{C_2F_4}$ pressure, $R_i\{\mathrm{CF_2O}\}$ increased linearly with increasing ozone pressure but became independent or even decreased at higher pressures of ozone. The experimental data although limited were interpreted on the basis of the rate equation

$$R_i\{\mathrm{CF_2O}\} = kk'[\mathrm{O_3}][\mathrm{C_2F_4}]^2/(1 + k'[\mathrm{C_2F_4}]) \qquad (\mathrm{XIII})$$

for which Heicklen obtained at 25 °C, $k = 300\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k' > 9 \times 10^4\ \mathrm{M}^{-1}$.

The investigation of Gozzo and Camaggi[91] was concerned primarily with the reaction stoichiometry and product identification. Their vapor-phase work appeared to be limited to the confirmation of eq XIII and most of their studies were conducted with solutions of inert halocarbon solvents at 0 °C. They employed a flow system with ozone in helium carrier gas and determined the reactant consumption and product formation in millimoles/hour. When the olefin was in excess (reactant ratio $[\mathrm{C_2F_4}]/[\mathrm{O_3}] \sim 50$), the major products were carbonyl fluoride and tetrafluoroethylene oxide. Traces of perfluorocyclopropane also appeared, but the reaction stoichiometry was best represented by

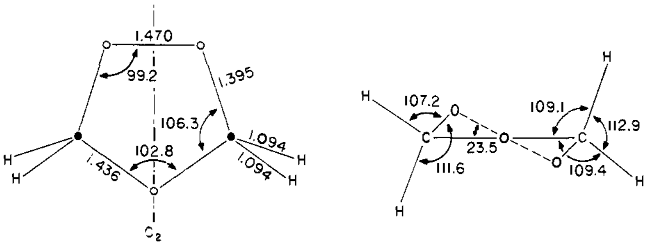


Figure 5. Microwave structure of secondary ethylene ozonide. From data of Gillies and Kuczkowski.[85,86]

$$2\mathrm{C_2F_4} + \mathrm{O_3} \rightarrow 2\mathrm{CF_2O} + \overline{\mathrm{CF_2CF_2O}} \qquad (56')$$

The product ratio $[\mathrm{CF_2O}]/[\overline{\mathrm{CF_2CF_2O}}]$ varied approximately as $2 + 8([\mathrm{O_3}]/[\mathrm{C_2F_4}])$. For reactant ratio $[\mathrm{C_2F_4}]/[\mathrm{O_3}]$ near unity, small amounts of secondary ozonide of $\mathrm{C_2F_4}$ were formed in addition to $\mathrm{CF_2O}$, $\overline{\mathrm{CF_2CF_2O}}$, and c-$\mathrm{C_3F_6}$. In these cases the reaction stoichiometry was that given by reaction 56 but the oxygen balance was poor owing to the formation of small quantities of polymer. The secondary ozonide of $\mathrm{C_2F_4}$ was reported to be a liquid at room temperature and to react with aqueous KI to give 1 mol of iodine, 2 mol of carbon dioxide, and 4 mol of fluoride ion. Its infrared spectrum has two intense bands near 1300 and 1200 cm^{-1}, and its mass spectrum has mass peaks corresponding to the ions $\mathrm{C_2F_4O_3}^+$, $\mathrm{C_2F_4O_2}^+$, and $\mathrm{C_2F_4O}^+$.

Later Gozzo et al.,[113] working in the gas phase at room temperature and at 15 °C in inert halocarbon solvents, identified a peroxidic liquid product essentially of structure $(\mathrm{CF_2CF_2OO})_n$. They explained this product as coming from the addition of the diradical ROO to $\mathrm{C_2F_4}$ followed by consecutive $\mathrm{O_2}$ and $\mathrm{C_2F_4}$ addition.

C_2Cl_4. The kinetics of the reaction between $\mathrm{O_3}$ and $\mathrm{C_2Cl_4}$ at 25 °C has been studied in the vapor phase by Mathias et al.,[5] and in $\mathrm{CCl_4}$ solution by Williamson and Cvetanović.[69] Although the latter investigators did not report the products of this reaction, in our laboratory[92] this reaction has been examined in the solid phase at liquid nitrogen temperature and in the liquid phase at reduced temperatures. In the solid phase, ozone did not react with $\mathrm{C_2Cl_4}$ but formed a π complex which has a weak characteristic infrared band at 1030 cm^{-1} and which decomposed reversibly into the reactants at about −130 °C. Similar π complexes have been observed before in many alkene and ozone solid-phase reactions.[88] No ozonides were formed in the liquid phase either. Vaporization of the liquid-phase products gave $\mathrm{CCl_2O}$ and $\mathrm{CCl_3CClO}$ as major products, tetrachloroethylene oxide as a minor product, and traces of HCOOH and a high-boiling polymer. The formation of the HCOOH was minimized by keeping our reaction vessel dry. The stoichiometry of the liquid-phase reaction could not be determined because of poor oxygen mass balance. However, the olefin consumption appeared to be accounted for by the $\mathrm{CCl_2O}$ and $\mathrm{CCl_3CClO}$ yields, and more phosgene than acid chloride was always produced.

The products of the gas-phase reaction at 25 °C were essentially the same as those observed from the liquid-phase study. However, traces of $\mathrm{Cl_2}$, CO, and $\mathrm{CO_2}$ were observed when the reaction was permitted to continue for long periods. Once again, it was not possible to determine the reaction stoichiometry but more products appeared to be formed when oxygen was used as the buffer gas. The reaction was too slow, ozone loss occurred through its own decomposition, the acid chloride slowly decayed with time, and the strongest infrared band of the minor product epoxide was obscured by an olefin infrared band. Figure 6 shows the variation in composition of a typical gas-phase reaction. The reaction was strongly inhibited by oxygen. The initial rates, $R_i\{\mathrm{CCl_2O}\}$ or $R_i\{\mathrm{CCl_3CCl(O)}\}$, determined by infrared

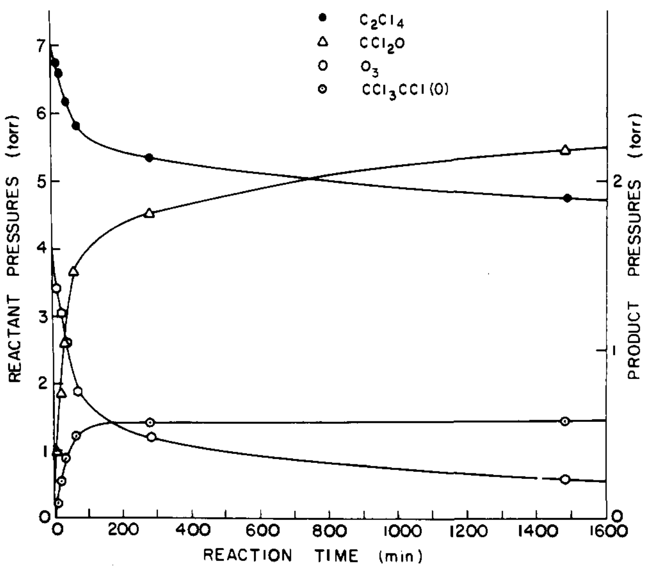


Figure 6. Time dependence of the composition of C_2Cl_4 ozonolysis reaction at 24 °C: $[C_2Cl_4]_0$ = 6.9 Torr, $[O_3]_0$ = 4.1 Torr. From Mathias et al.[5] with permission of the National Research Council of Canada.

spectroscopy, increased with olefin pressures but were not affected much by nitrogen buffer gas or the initial ozone pressure (range of a factor of 2). A log–log plot of initial rates against olefin pressures (range of a factor of 5) gave a slope of 1.8, and the average value of $R_i\{CCl_2O\}/R_i\{CCl_3CClO\}$ was 1.3. With O_2 buffer, the initial rate was decreased by a factor of at least 10.

Williamson and Cvetanović[69] found that the reaction rate in CCl_4 solution at 25 °C was first order in both $[O_3]$ and $[C_2Cl_4]$. The concentration of olefin which was always in excess was varied in the range of 1-5 mmol/l., and the ozone ultraviolet band at 0.280 μm was used to follow the rate. Under these conditions the second-order rate constant was 1.0 M^{-1} s^{-1}.

$CHClCCl_2$. Only Williamson and Cvetanović[69] studied this reaction. In CCl_4 solution at 25 °C, the rate was reported to be first order in each reactant with the second-order rate constant being 3.6 M^{-1} s^{-1}. The products of the reaction or their stoichiometries are not known.

CH_2CCl_2. The products of the vapor-phase reaction at 25 °C have been identified by Hull et al.[70] to be CCl_2O, HCOOH, $CH_2ClCCl(O)$, CO, CO_2, O_2, HCl, and possibly water although it was never detected. The yield of phosgene was always either comparable to or greater than the yield of formic acid, and the sum of the phosgene and acid chloride yields was generally slightly less than the consumption of the olefin. Presumably, the hydrolysis of the acid chloride led to the latter inequality. The consumption ratio [olefin]/$[O_3]$ was approximately unity when the reactant pressures were comparable but this ratio approached two as the olefin was made more in excess. With O_2 buffer gas, the limiting consumption ratio was near five for high excess olefin runs. On the other hand, the yield of CCl_2O per mole of O_3 with N_2 buffer appeared to be independent of the relative amounts of the reactants and varied in the range of 0.3 to 0.4. The same mole ratio increased to near unity in oxygen buffer when the olefin was made more excess.

In CCl_4 solutions at 25 °C, Williamson and Cvetanović[69] found that the yield of phosgene per reactant olefin consumed was essentially quantitative (GC analysis). However, the only other product observed was a white solid which remained after solvent evaporation and which exploded violently on attempt to collect the material. In the low-temperature solid-phase reaction,[92] on the other hand, both CCl_2O and $CH_2ClCCl(O)$ have been identified. Infrared analysis of the solid reactants showed initially the reversible formation of a π complex, and on further warming to about −90 °C only the infrared bands due to phosgene and acid chloride appeared. Vaporization of the reaction mixture showed unreacted olefin, CCl_2O, $CH_2ClCCl(O)$, and HCOOH.

When olefin was in excess, the rate of ozonolysis of CH_2CCl_2 at 25 °C in CCl_4 solution was found to consume equal amounts of reactants, to be first order in each reactant, and to have a rate constant of 22.1 M^{-1} s^{-1}.[69] The kinetics is more complex in the vapor phase at the same temperature, for Hull et al.[70] determined the rate law to be

$$-d[O_3]/dt = -d[CH_2CCl_2]/dt = k_{XIV}[CH_2CCl_2][O_3]^2 \quad (XIV)$$

with N_2 buffer gas, and

$$-d[O_3]/dt = k_{XV}[CH_2CCl_2][O_3] \quad (XV)$$

when oxygen gas was used as buffer. In these studies the ozone pressure was a Torr or less and the olefin was varied from 3 to 100 Torr. The experimental values of the rate constants were $k_{XIV} = (2.4 \pm 0.6) \times 10^6\ M^{-2}\ s^{-1}$ and $k_{XV} = 2.2 \pm 0.6\ M^{-1}\ s^{-1}$. With O_2 buffer, the second-order rate constant for eq XV obtained from the decay of an olefin infrared band or the combined rate of appearance of phosgene and acid chloride bands was almost a factor of 2 greater. Also, the value of 2.2 M^{-1} s^{-1} was an average of k_{XV} values which appeared to decrease systematically by a factor of almost 2 as the olefin pressure was increased from 8 to 100 Torr. In addition, with both N_2 and O_2 buffers, the initial rates appeared to be somewhat faster than the rates predicted by the rate equations XIV and XV when the olefin pressures were low.

CHClCHCl (DCE). The stoichiometry of the gas-phase reaction between *cis-* or *trans-*DCE and ozone at 23 °C has been established quantitatively by Blume et al.[71] to be as given by the reaction

$$2CHClCHCl + 2O_3 \rightarrow 4HCClO + O_2 \quad (57)$$

The reactant pressures were measured directly, the oxygen concentrations were determined by gas chromatography after completion of the reaction, and the unstable formyl chloride[93] concentrations were established spectroscopically. Since the formyl chloride was known to decompose to HCl and CO with a half-life of about 10–20 min, the products of reaction 57 were allowed to stand until the formyl chloride infrared bands disappeared. From the infrared determination of the absolute concentration of CO and from the known reactant pressures and initial absorbance of HCClO, the absorption coefficients of the HCClO infrared bands were calculated. The two most intense bands of this molecule are the carbonyl stretch at 1784 cm^{-1} and the CCl stretch at 739 cm^{-1}.[93] The decadic absorption coefficients of the R-branches of these bands were found to be 0.0194 and 0.0129 $Torr^{-1}$ cm^{-1}, respectively.[71] In addition to HCClO, O_2, HCl, and CO, traces of CCl_2O and HCOOH were observed in some of the reaction mixtures. The latter two species evidently came from hydrolysis reactions, for it was possible to minimize their formation by careful pumping of the reaction vessels.

The stoichiometry for the ozonolysis of *cis*-DCE in CCl_4 solution at 25 °C was examined by Williamson and Cvetanović.[69] They determined the consumption ratio [DCE]/$[O_3]$ to be one but were able to identify only one product from the gas chromatographic analysis. This product was phosgene, and 0.18 mol of it was reported to be generated from each mole of DCE consumed. These investigators reported, however, that with 50% completion of the reaction three other GC peaks appeared whose retention times were shorter than that for CCl_2O and whose relative peak areas changed with time. In the study of the liquid phase[71] formed by allowing the solid reactants to melt at reduced temperatures, HCClO was observed as the major product with only traces of HCOOH and CCl_2O. Small amounts of explosive clear liquid also remained after evaporation of the liquid mixture. The decomposition of HCClO in the liquid phase was very much faster than the gas-phase rate, but HCl and CO

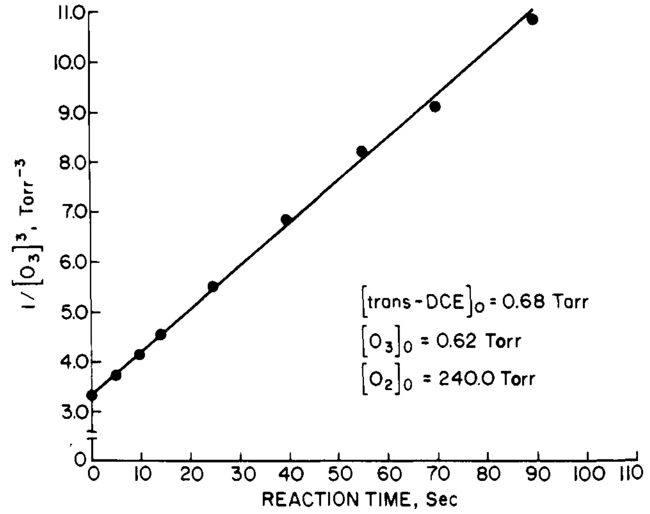


Figure 7. Fourth-order kinetic plot of *trans*-CHClCHCl reaction with ozone at 23 °C. From Blume et al.,[71] with permission of John Wiley & Sons.

were still the products. The three unidentified GC peaks observed by Williamson and Cvetanović may very well have been HCClO, HCl, and CO. The reaction in the low-temperature solid phase gave essentially the same products[92] as those observed in the liquid phase. Only a π complex and no ozonides were observed as the solid reactants were allowed to warm slowly. At temperatures above about −150 °C, absorption bands due to solid HCClO grew. Formyl chloride began to sublime off the low temperature window at about −110 °C.

Relatively simple kinetics was observed by Williamson and Cvetanović[69] for the ozonolysis of DCE in CCl_4 solution at 25 °C. The rate was first order in each reactant with the second-order rate constant being 35.7 M^{-1} s^{-1} for *cis*-DCE and 591 M^{-1} s^{-1} for the trans isomer. Thus, in CCl_4 solution at 25 °C the reactivity toward ozone of *trans*-DCE is about 17 times faster than that of the *cis*-DCE which in turn reacts about six times faster than does 1,1-DCE. The kinetics in the gas phase, on the other hand, was expected to be complex since reaction 57 under excess olefin condition caused the isomerization of the reactant in addition to giving the products formyl chloride and oxygen.[93] Subsequent studies by Blume et al.[71] have shown indeed that reaction 57 has an exceedingly complex kinetics.

Blume et al. used infrared and ultraviolet spectroscopy to follow the rates of reaction 57. Olefin pressures ranged from 0.2 to 40 Torr for *cis*-DCE and from 0.3 to 80 Torr for *trans*-DCE. Ozone pressures were limited to below about 7 Torr. Rates were also determined with the reactants buffered with N_2 and O_2 gas. It was found experimentally that the rates of reaction 57 satisfied the condition $R = -d[DCE]/dt = -d[O_3]/dt = +d[HCClO]/2dt$ and could be expressed in the general form

$$R = k_{XVI}[DCE]^n[O_3]^m \qquad (XVI)$$

where n and m had values of 1 or 2 depending on the pressure range of each reactant. When the pressures of O_3 and DCE were both of the order of 1 Torr or less, it was found that $n = m = 2$. Figure 7 illustrates a kinetic plot of such a reaction in which $[trans\text{-DCE}] = [O_3] = 0.62$ Torr so that $1/[O_3]^3$ plotted against reaction time gave a straight line. Also, when one or the other reactant was in excess, second-order kinetic plots were obtained by following the reactant not in excess. However, in excess ozone kinetic runs with $[O_3]$ greater than about 3 Torr, $n = 2$ was still satisfied but the fourth-order rate constant with $m = 2$ decreased as the ozone pressures were increased. In these kinetic runs more constant rate coefficients were obtained by taking $m = 1$. Finally, when the olefin was in excess and [DCE] was greater than about 4 Torr, both exponents became $n = m = 1$.

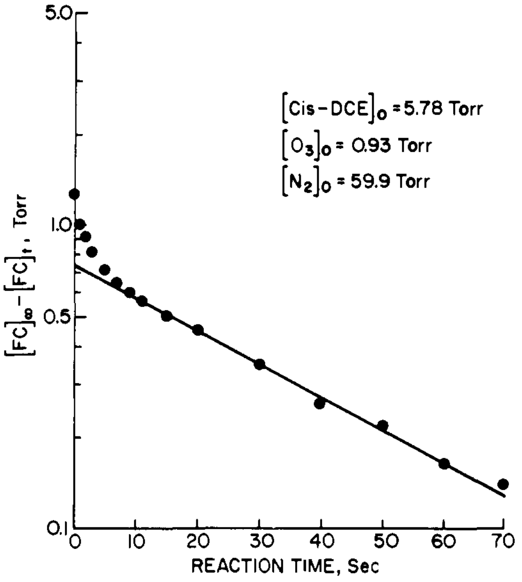


Figure 8. First-order kinetic plot of *cis*-CHClCHCl reaction with ozone at 23 °C in N_2 buffer. From Blume et al.,[71] with permission of John Wiley & Sons.

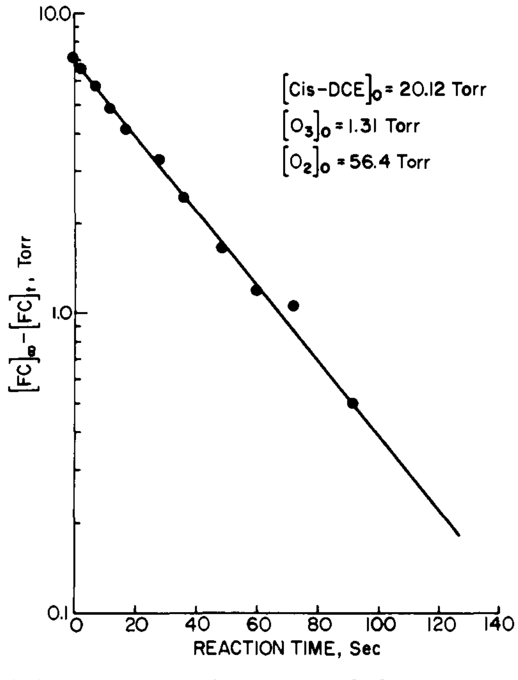


Figure 9. First-order kinetic plot of *cis*-CHClCHCl reaction with ozone at 23 °C in O_2 buffer. From Blume et al.[71] with permission of John Wiley & Sons.

Figure 8 shows a first-order plot of an excess *cis*-DCE reaction in which the formation of HCClO was followed. With N_2 buffer, the rates were invariably faster at the beginning of the reaction as is apparent in Figure 8, but the rates soon followed first-order kinetics. Such initial deviations were absent when O_2 buffer was used as illustrated in Figure 9. Moreover, the second-order rate constants obtained from the final first-order kinetic section of the N_2-buffered reactions were the same within experimental uncertainty limits as the second-order rate constants derived from the O_2 buffered reactions. Also, under all reactant pressure conditions, rate constants obtained from reactions with O_2 buffer were always less by as much as a factor of 10 than the initial rate constants from the N_2-buffered reactions. Numerical values of the various experimental rate constants are summarized in Table XI. There were considerable uncertainties due to the limited pressure ranges in which the rates could be determined, but the

TABLE XI. Kinetic Data for the Ozonolysis of 1,2-Dichloroethylene (DCE)

Solvent and temp	Concentration	Rate equation	Rate constants[a]	Source
CCl_4 soln, 25 °C	$[O_3] \ll [DCE] = 1 \times 10^{-3} - 5 \times 10^{-3}$ M	$R\{O_3\} = k[DCE][O_3]$	cis 35.7 $M^{-1}\,s^{-1}$ trans 591 $M^{-1}\,s^{-1}$	Williamson and Cvetanovi]c[69]
$N_2(O_2)$ gas, 23 °C	$[DCE] \cong [O_3]$ <1 Torr	$R\{DCE\} = R\{O_3\} = k[DCE]^2[O_3]^2$	cis 1.23 × 10^{11} $M^{-3}\,s^{-1}$ (0.12 × 10^{11} $M^{-3}\,s^{-1}$) trans 13.1 × 10^{11} $M^{-3}\,s^{-1}$ (4.0 × 10^{11} $M^{-3}\,s^{-1}$)	Blume et al.[71]
	$[DCE] \leqq 1$ Torr $[O_3] \lesssim 2$ Torr	$R\{DCE\} = k[DCE]^2[O_3]$	cis 2.4 × 10^7 $M^{-2}\,s^{-1}$ (0.146 × 10^7 $M^{-2}\,sec^{-1}$) trans 3.2 × 10^7 $M^{-2}\,s^{-1}$ (0.59 × 10^7 $M^{-2}\,s^{-1}$)	
	$[DCE] > 3$ Torr $\gg [O_3]$	$R\{O_3\} = k[DCE][O_3]$	cis 4.6 × 10^2 $M^{-1}\,s^{-1}$ (0.37 × 10^2 $M^{-1}\,s^{-1}$) trans 9.0 × 10^2 $M^{-1}\,s^{-1}$ (2.3 × 10^2 $M^{-1}\,s^{-1}$)	

[a] Rate constants enclosed in parentheses are from O_2-buffered reactions.

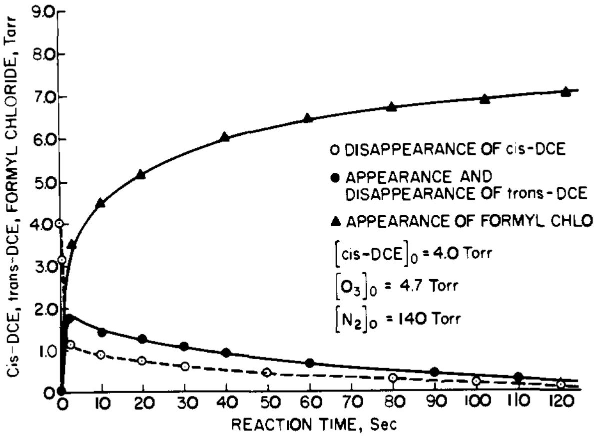


Figure 10. Ozone-catalyzed isomerization of *cis*-CHClCHCl at 23 °C. From Blume et al.[71] with permission of John Wiley & Sons.

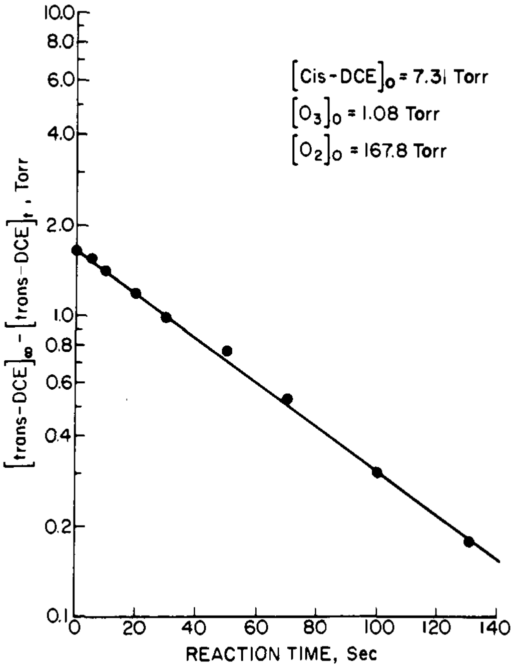


Figure 11. First-order kinetic plot from the isomerization data for the *cis*-CHClCHCl reaction at 23 °C with O_2 buffer. From Blume et al.,[71] with permission of John Wiley & Sons.

trans-DCE definitely reacted faster than did the cis isomer.

It was already pointed out that the reaction under excess olefin conditions led to some isomerization of the reactant olefin. Similar isomerizations were observed even in excess ozone runs provided the olefin pressures were reasonably high. Figure 10 illustrates the experimental results from such a case. Here, the pressure variations of the reactant *cis*-DCE and the products *trans*-DCE and HCClO were determined from three separate experiments in which the reactant pressures were comparable. It is evident from this figure that the isomerization reaction appears to be faster than the ozonolysis reaction. In excess *cis*-DCE with ozone pressures of about 1 Torr, the yield of trans isomer appeared to increase from 20% to about 30% as the olefin pressure was increased from 6 to 40 Torr. On the other hand, with a similar pressure of ozone only 3–4 Torr of cis isomer was formed from excess *trans*-DCE even though its pressures were varied from 6 to 20 Torr. Although it was not experimentally feasible to study the kinetics of isomerization of the olefin, the isomerization rates appeared to be a measure of the rates of ozone disappearance as illustrated in Figure 11. In this run, 1.72 Torr of *trans*-DCE and 4.58 Torr of *cis*-DCE were observed at the end of the reaction, so that 7.31 − 1.72 − 4.58 = 1.01 Torr of reactant olefin was consumed while the initial pressure of O_3 was 1.08 Torr.

CHClCH₂. Vinyl chloride also was one of the chloroethylenes examined by Williamson and Cvetanović.[69] They found that 1.2 mol of CH_2CHCl was consumed for each mole of ozone during the ozonolysis in CCl_4 solution at 25 °C, but the only reaction product identified by gas chromatography was 0.06 mol of phosgene/mol of olefin consumed. The reaction rate was observed to be first order in each reactant and to have a second-order rate constant of 1.18 × 10^3 $M^{-1}\,s^{-1}$.

In the infrared spectroscopic study of vinyl chloride ozonolysis, currently in progress in our laboratory, Kolopajlo[94] observed no CCl_2O among the products. Instead the primary products from both the gas and liquid phase reactions were formic acid and formyl chloride. Furthermore, the reaction stoichiometry appeared to be represented by

$$CH_2CHCl + O_3 \rightarrow HCOOH + HCClO \qquad (58)$$

The reaction in the solid phase at low temperatures gave more informative results.[92] The 1030-cm^{-1} region where the olefin–ozone π complexes absorb[88] was obscured by the infrared bands of the reaction products and by an olefin band, so the presence of a π complex in this case could not be verified. However, as the solid reactants were warmed to about −165 °C, two sets of new absorption bands started to appear. Repeated warming of the solid sample to about −150 °C caused the bands of both sets to grow at the same rate. One set of bands was readily identified as belonging to formyl chloride,[93] and this

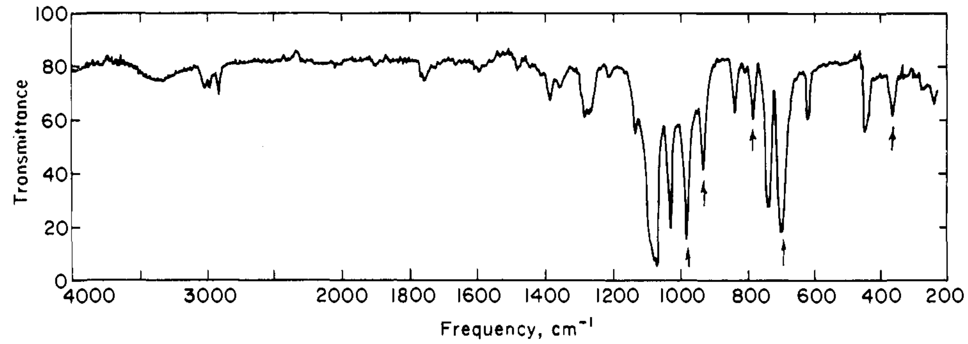


Figure 12. Infrared spectrum of vinyl chloride primary ozonide at liquid nitrogen temperature. The absorption bands identified by arrows are assigned to the more stable isomer of the ozonide. The weak band at 1755 cm^{-1} is due to formyl chloride residue still in the ozonide sample. From Hisatsune et al.[92]

compound began to sublime off the low-temperature infrared window at about −120 °C. The second set of bands which is illustrated in Figure 12 has been assigned to the primary ozonide of vinyl chloride. This ozonide was found to be stable to about −55 °C, above which it decomposed irreversibly into formic acid, formyl chloride, and a somewhat volatile polymer. Interestingly, the infrared spectrum of the latter polymer was essentially the same as that of the peroxidic polymer observed in the decomposition of ethylene primary ozonide.[88]

The spectrum shown in Figure 12 has a strong resemblance to those of primary and secondary ethylene ozonides illustrated in Figure 4. Bands near 1000 cm^{-1} are presumably due to O–O and C–O bond stretching modes, but there are two intense bands near 700 cm^{-1} where the C–Cl stretch band is expected. Although these bands grew at the same rate as the primary ozonide was being formed, during the decomposition their relative intensity ratios were no longer constant. Thus, these bands evidently represent the expected two isomers[95] of the vinyl chloride primary ozonide, but the assignment of each peak to the axial C–Cl or the equatorial C–Cl stretch in the puckered, five-membered trioxa ring is not apparent. Nevertheless, the ozonide with the lower C–Cl stretch frequency appeared to be the more stable isomer, and other bands associated with this species are identified by arrows in Figure 12.

The kinetics of the ozonolysis of vinyl chloride in the gas phase is also under investigation in our laboratory.[94] Preliminary studies have shown that this reaction appears to be too fast for spectroscopic study without oxygen buffer gas. With oxygen, however, the reaction is strongly inhibited and its rate can be followed conveniently by ordinary spectroscopic instruments. The results from one such kinetic run are displayed in Figure 13. Here the pressures of vinyl chloride and ozone are similar, and a plot of the inverse of vinyl chloride pressure is essentially a linear function of time. Thus, the rate under these particular experimental conditions is first order in each reactant. The resulting second-order rate constant is 3.9 M^{-1} s^{-1} at 22 °C which is three orders of magnitude smaller than the rate constant for the same reaction in CCl_4 solution at 25 °C in the absence of O_2.

B. Review of Ozonolysis Mechanisms

C_2H_4. The recent experimental data for the condensed phase reactions of ethylene and ozone are still consistent with the Criegee mechanism[96] of olefin ozonolysis, which can be represented by the following sequence of reactions:

$$CH_2CH_2 + O_3 \rightarrow \overline{CH_2CH_2OOO} \qquad (59)$$

$$\overline{CH_2CH_2OOO} \rightarrow H_2C^+OO^- + CH_2O \qquad (60)$$

$$H_2C^+OO^- + CH_2O \rightarrow \overline{CH_2OCH_2OO} \qquad (61)$$

$$H_2C^+OO^- \rightarrow HCOOH \qquad (62)$$

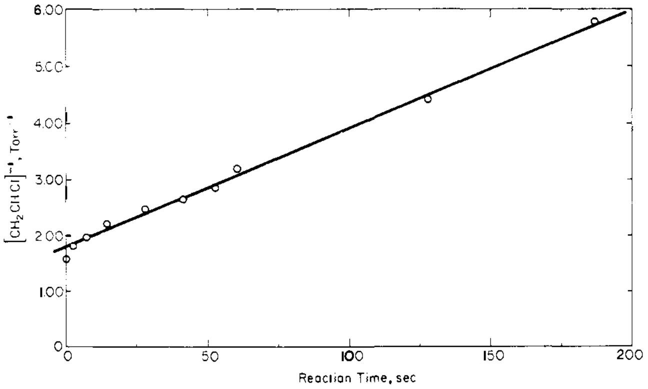
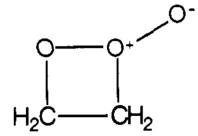
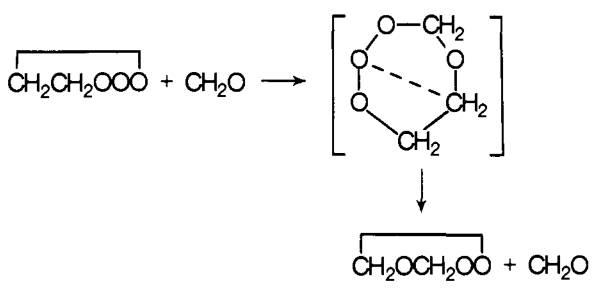


Figure 13. Second-order kinetic plot of vinyl chloride reaction with ozone at 22 °C. From Kolopajlo.[94]

The low-temperature infrared studies of Hull et al.[88] have shown that the first stable product formed by reaction 59 near liquid nitrogen temperature was the primary ozonide 1,2,3-trioxacyclopentane. Further warming of the solid sample to about −100 °C caused the primary ozonide to change smoothly into the secondary ozonide which remained stable to room temperature. In the vapor phase at temperatures above about 50 °C, the secondary ozonide was observed to decompose[89] by a first-order process to give formaldehyde and formic acid. The formation of the zwitterion in reaction 60 was inferred by the small amounts of polymeric peroxides observed after completion of each experiment. Minor amounts of HCOOH and CH_2O were also observed in the solid-phase reaction. The HCOOH could come from reaction 62 or the formation of energetic secondary ozonide via reaction 61 followed by decomposition prior to stabilization. The simultaneous formation of both the primary and secondary ozonides during the initial warming sequence also indicated that reaction 59 must be exothermic. The enthalpy change for the corresponding reaction 59 with 1-butene has been estimated by O'Neal and Blumstein[97] to be about −47 kcal/mol. Kuczkowski and coworkers[85-87] have provided a convincing demonstration of reactions 60 and 61 in the liquid phase ozonolysis by showing that the isotopic oxygen atom from the reactant CH_2O entered exclusively the epoxy position in the secondary ozonide, and that no labeled oxygen entered the peroxy position as previously reported.[98,99] Thus, it appears unnecessary in the present sequence of reactions to invoke, as Story and coworkers[100,101] have proposed in other ozonolysis studies, the Staudinger primary ozonide[102] as a precursor to the 1,2,3-





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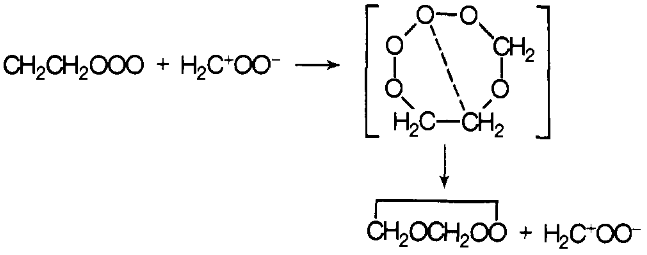


(64)

trioxacyclopentane, or the additional reaction paths[103] for the formation of the secondary ozonide shown in eq 63 and 64.

The low-temperature spectroscopic studies of Hull et al.[88] appear to clarify one other aspect of reaction 59, and this concerns the precursor, if any, to the primary ozonide. Vrbaski and Cvetanović[76] apparently were the first to propose for the ozonolysis of an aliphatic double bond that a π complex may be formed in equilibrium with the reactants according to reaction 65 and that the subsequent rearrangement of this complex by reaction 66 was the source of the primary ozonide.

$$CH_2CH_2 + O_3 \rightleftarrows CH_2CH_2{\cdot}O_3(\pi) \qquad (65)$$

$$CH_2CH_2{\cdot}O_3(\pi) \rightarrow \overline{CH_2CH_2OOO} \qquad (66)$$

Story et al.[103] have also included type 65 and 66 reactions in their ozonolysis mechanism but not as a reversible step 65. Bailey et al.[104] have described the 66-type reaction as a 1,3-dipolar cycloaddition and have included additional decay steps for the π complex to account for the expoxides and free radical products observed in many ozonolysis reactions. These additional steps in the present case would be as follows.

$$CH_2CH_2{\cdot}O_3(\pi) \rightarrow CH_2CH_2{\cdot}O_3(\sigma) \rightarrow \text{epoxides} \qquad (67)$$

$$CH_2CH_2{\cdot}O_3(\pi) \rightleftarrows CH_2CH_2O_3\ \text{(free radical zwitterion)} \qquad (68)$$

↳ radical chain carrier

Carles and Fliszár,[105] on the other hand, proposed two parallel paths to the primary ozonide formation, namely, the direct path reaction 59 and the sequential reactions 65 and 66 in which the complex could be either a π or a σ complex.

A common feature in all these proposed mechanisms is that the precursor of the primary ozonide is the π complex. Although such a π complex was not observed in the case of ethylene, the low-temperature studies[88] revealed their presence in all other olefin and ozone reaction systems and in toluene–ozone systems as well. It appears very probable that the negative results with ethylene were not due to the real absence of such a complex but to the temperature limitation in the low-temperature cell used in the experiments. Thus, on the basis of the results from other olefins, one may conclude that reaction 65 is correct and that the complex must be a charge-transfer type π complex. However, in no instance were the π complexes of other simple olefins observed to give the primary ozonides. Instead, they decomposed reversibly to the original olefin and ozone. Hence, reaction 66 did not appear to occur in the condensed phases and the formation of the primary ozonide was by the direct reaction 59. Also, the products observed in these condensed-phase reactions indicated that reactions 67 and 68 were not important. In summary, the ozonolysis of ethylene in the liquid and solid phases can be described adequately by the mechanism consisting of reactions 59 through 62 and reaction 65.

The mechanism for the gas-phase ozonolysis of ethylene, on the other hand, still remains unclear primarily because of insufficient data and because of the experimental difficulties in getting such data. For example, information on even the reaction products is not adequate, and species which have been identified experimentally appear to be limited to HCOOH,[77] CH_3CHO,[77] aerosol of unknown composition,[80] and, under low-pressure chemiluminescent conditions,[73] vibrationally excited OH and electronically excited CH_2O and OH. However, more data on product analysis are available for olefins of higher molecular weights, and on the basis of such results two mechanisms have been proposed. One mechanism, which is still essentially the Criegee mechanism, suggests that reactions 59 and 60 occur rapidly and subsequent reactions initiated particularly by CH_2OO lead to the observed products. Here, the species CH_2OO may react as a zwitterion[76,106] or as a diradical.[73] For example, the diradical may add to the ethylene and by a single or multiple steps lead to CH_2O and the observed rearrangement product CH_3CHO. The zwitterion may rearrange into HCOOH or react with oxygen[106] to produce hydroxyl and performate free radicals, both of which can initiate other free radical reactions.

The second mechanism is that due to O'Neal and Blumstein,[97] and it was proposed principally to account for the energy requirements in chemiluminescent reactions and for the products such as α-diketones which are difficult to explain by the Criegee mechanism. These authors suggested that the primary ozonide formed in reaction 57 is in equilibrium with an opened-ring diradical species which for ethylene would be as follows

$$\overline{CH_2CH_2OOO} \rightleftarrows {\cdot}OCH_2CH_2OO{\cdot} \qquad (69)$$

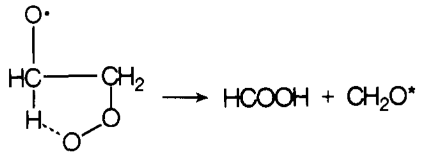
The diradical may then dissociate to give the normal Criegee products of reaction 60, or it may undergo an intramolecular α-hydrogen abstraction reaction to give an α-keto hydroperoxide.

$${\cdot}OCH_2CH_2OO{\cdot} \rightarrow CH_2OO + CH_2O \qquad (70a)$$

$$\rightarrow OCHCH_2OOH \qquad (70b)$$

The hydroperoxide may decompose into the normal ozonolysis products, HCOOH and CH_2O, or into water and glyoxal (α-diketone), or produce an OH radical and an oxy-free radical. O'Neal and Blumstein also estimated the energetics of reactions 70a and 70b and concluded that for ethylene and propylene the diradical should decay mainly by step 70a while for 1-butene and other olefins with greater internal degrees of freedom reaction 70b should dominate. Consequently, secondary ozonides should not be the major products from the latter ozonolysis reactions particularly at higher total pressures. The low-temperature infrared studies,[88] on the other hand, revealed that not only ethylene and propylene but 2-butenes also gave secondary ozonides. Although O'Neal and Blumstein suggested that reaction 63 may be the source of any unexpected secondary ozonides, the isotopic studies by Kuczkowski and coworkers[85-87] appear to rule out this possibility. It seems that the estimates of energetics of these ozonolysis reactions may not be completely valid or additional modifications of the reaction mechanism may be necessary.

A further shortcoming of the O'Neal–Blumstein mechanism is that internal β-hydrogen abstraction by the diradical was suggested to explain the chemiluminescence of O_3–olefin reactions. Of course, in the C_2H_4 system there is no β hydrogen. Finlayson et al.[73] modified the O'Neal–Blumstein mechanism to suggest that electronically excited CH_2O was produced by α-hydrogen abstraction

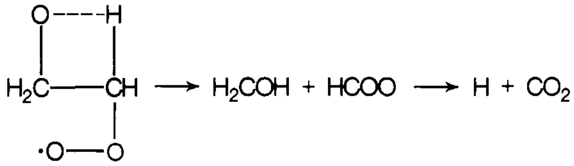


(71)

but this route seems unlikely from both energetic and steric considerations. The experimental evidence clearly requires the presence of free H atoms, and Finlayson et al.[73] suggested two routes, both of which are variations of sequential H-atom splitting from the zwitterion

$$H_2COO \rightarrow HCOOH^* \rightarrow H + HCOO \rightarrow H + CO_2 \quad (72)$$

Again, these routes seem unlikely to us, and we prefer hydrogen abstraction by the single O atom in the diradical



(73)

The proposed routes for electronically excited OH production were[73]

$$O + H \rightarrow OH^*$$

$$O + HCO^{\ddagger} \rightarrow OH^* + CO$$

However, at this time the proposed routes to chemiluminescence must all be considered to be speculative.

Until very recently[73,83] the only investigation that indicated that the second-order kinetics of the gas-phase ethylene ozonolysis was different in the absence and presence of O_2 was by Wei and Cvetanović.[78] Herron and Huie[83] noted instead that the experimental results were nonreproducible, and much larger second-order rate constants were obtained when the reaction was carried out in argon buffer gas. However, with added O_2, rate constants which agreed with earlier literature values (in the presence of O_2) were obtained. In the case of propylene, Herron and Huie showed that the second-order rate constant decreased by a factor of almost 2 as the O_2 pressure was increased to about 1 Torr and thereafter remained constant on further increase in O_2. This limiting rate constant was found to agree closely with those reported by earlier investigators (see Table IX). On the basis of these results and those reported by other investigators, Herron and Huie proposed a schematic free radical mechanism for the ozonolysis reaction.

$$O_3 + C_2H_4 \rightarrow P^* \quad (74)$$

$$P^* \rightarrow Q + R + \ldots \quad (75)$$

$$P^* + M \rightarrow P + M \quad (76)$$

$$O_3 + (Q + R + \ldots) \rightarrow \text{products} \quad (77)$$

$$O_2 + (Q + R + \ldots) \rightarrow \text{products} \quad (78)$$

Here, P* was reported to be an adduct which is not necessarily formed initially but could be formed by a subsequent rearrangement.

C_2F_4. A simple mechanism involving an ozone–olefin adduct was proposed by Heicklen[1,68] to account for the limited experimental data available for this ozonolysis reaction.

$$C_2F_4 + O_3 \rightleftarrows C_2F_4O_3 \quad (79)$$

$$C_2F_4O_3 + C_2F_4 \xrightarrow{O_3} 4CF_2O + O_2 \quad (80)$$

The nature of the initial adduct in reaction 79 was not specified but reaction 80 was proposed originally[68] to be composite and to involve intermediates such as CF_2, $(CF_2O)_2$, and C_2F_4O. Later,[1] reaction 80 was represented by the following sequence of steps.

$$C_2F_4O_3 + C_2F_4 \rightarrow C_2F_4O + C_2F_4O_2 \quad (81)$$

$$C_2F_4O_2 \rightarrow 2CF_2O \quad (82)$$

$$C_2F_4O + O_3 \rightarrow C_2F_4O_2 + O_2 \quad (83)$$

Whichever multiple steps reaction 80 may involve, the rate equation resulting from reactions 79 and 80 is

$$R\{CF_2O\} = \frac{4k_{79}k_{80}[O_3][C_2F_4]^2}{k_{-79} + k_{80}[C_2F_4]} \quad \text{(XVII)}$$

Comparison with the experimental rate equation gave $k_{79} = 300$ $M^{-1}\,s^{-1}$, $k_{80}/k_{-79} > 9 \times 10^4\ M^{-1}$ and $k_{79}k_{80}/k_{-79} > 3 \times 10^7$ $M^{-2}\,s^{-1}$ at 25 °C. However, this rate equation did not account for the observation that the rate became independent of $[O_3]$ or actually decreased at high ozone pressures.

Gozzo and Camaggi[91] included additional steps to the Criegee mechanism to explain the observed solution phase reaction products: CF_2O, the epoxide $\overline{CF_2CF_2O}$, c-C_3F_6, and traces of secondary ozonide.

$$C_2F_4 + O_3 \rightarrow [C_2F_4O_3] \rightarrow CF_2O + CF_2OO \quad (84)$$

$$CF_2OO + C_2F_4 \rightarrow \overline{CF_2CF_2O} + CF_2O \quad (85)$$

$$2CF_2OO \rightarrow 2CF_2O + O_2 \quad (86)$$

$$CF_2OO \rightarrow CF_2 + O_2 \quad (87)$$

$$CF_2 + C_2F_4 \rightarrow c\text{-}C_3F_6 \quad (88)$$

However, these investigators also observed only CF_2O in the gas-phase reaction, so the gas-phase mechanism evidently consists of just reactions 84 and 86. Hence, the rate $R\{CF_2O\}$ will be first order in each reactant, a result in accord with Heicklen's[1,68] high-pressure limit. The reaction in the solution phase gave CF_2O and tetrafluoroethylene oxide as the major products, so in this case Guzzo and Camaggi considered only steps 84, 85, and 86. A steady-state approximation for CF_2OO gives

$$\frac{d[CF_2O]}{d[\overline{CF_2CF_2O}]} = 2 + \frac{2k_{84}k_{86}[O_3]}{k_{85}{}^2[C_2F_4]} \quad \text{(XVIII)}$$

with $k_{84}k_{86}/k_{85}{}^2$ being about 4.

C_2Cl_4. On the basis of kinetic data from all the chloroethylenes studied in CCl_4 solutions, Williamson and Cvetanović[69] proposed the following general mechanism for the ozonolysis of these olefins RR′.

$$RR' + O_3 \rightarrow \text{product I} \quad (89)$$

$$RR' + O_3 \rightleftarrows RR'{\cdot}O_3 \quad (90)$$

$$RR'{\cdot}O_3 \rightarrow \text{product II} \quad (91)$$

Here, reaction 89 was described as a one-step process giving product I which does not return to the reactants. The complex formed in reaction 90 may return to the reactants with no geometric isomerization, or it may decompose irreversibly according to reaction 91. In these reactions the products I and II are some intermediates of the reaction and not necessarily the final products. With this mechanism, the observed second-order rate constant was related to the elementary constants as follows:

$$k_{\text{exptl}} = k_{89} + (k_{90}k_{91}/k_{-90})/(1 + k_{90}/k_{-90}) \quad \text{(XIX)}$$

Although the experimental data were too limited to determine the relative importance of the one- and two-step terms in eq XIX, Williamson and Cvetanović suggested the possibility that reaction 89 may lead to the primary ozonide while reactions 90 and 91 may correspond to the oxygen-transfer process observed, for example, in the ozonolysis of ethylene where CH_3CHO was produced. We have already quoted the second-order rate constants obtained by Williamson and Cvetanović during the review of each haloethylene, but these constants are summarized together in Table XII.

TABLE XII. Second-Order Rate Constants for the Reactions of Ozone with Haloethylenes in CCl_4 Solution at 25 °C[a]

Haloethylene	k_{exptl}, $M^{-1}\,s^{-1}$	Haloethylene	k_{exptl}, $M^{-1}\,s^{-1}$
CCl_2CCl_2	1.0	*cis*-CHClCHCl	35.7
$CHClCCl_2$	3.6	*trans*-CHClCHCl	591
CH_2CCl_2	22.1	CH_2CHCl	1180

[a] From Williamson and Cvetanović.[69]

A more elaborate mechanism was necessary to interpret the gas-phase results obtained by Mathias et al.[5] The initial step in this mechanism, shown below, gave the diradical Criegee product CCl_2OO which propagated a chain reaction

$$C_2Cl_4 + O_3 \rightarrow CCl_2O + CCl_2OO \qquad (92)$$

$$CCl_2OO + O_3 \rightarrow CCl_2O + 2O_2 \qquad (93)$$

$$CCl_2OO + C_2Cl_4 \rightarrow CCl_2OO_2{\cdot}C_2Cl_4 \qquad (94)$$

$$CCl_2OO{\cdot}C_2Cl_4 + O_3 \rightarrow CCl_2OO{\cdot}C_2Cl_4{\cdot}O_3 \qquad (95a)$$

$$\rightarrow CCl_2OO + C_2Cl_4O + O_2 \qquad (95b)$$

$$CCl_2OO{\cdot}C_2Cl_4{\cdot}O_3 + C_2Cl_4 \rightarrow CCl_2OO + 2CCl_2O + C_2Cl_4O \qquad (96)$$

In this mechanism, C_2Cl_4O formed in steps 95b and 96 represented both the epoxide $\overline{CCl_2CCl_2O}$ and the rearranged product $CCl_3CCl(O)$. Application of steady-state approximations to the intermediates leads to the following initial rates, $R_i\{X\}$

$$R_i\{CCl_2O\} = 2k_{92}[O_3][C_2Cl_4] + 2\left(\frac{k_{92}k_{94}k_{95a}}{k_{93}k_{95}}\right)[C_2Cl_4]^2 \qquad (XX)$$

$$R_i\{C_2Cl_4O\} = \frac{k_{92}k_{94}}{k_{93}}[C_2Cl_4]^2 \qquad (XXI)$$

For long chains, only the second term in eq XX is important so that the $R_i\{CCl_2O\}$ should be second order in $[C_2Cl_4]$ and independent of $[O_3]$. Experimentally, the olefin order was about 1.8 and no O_3 dependence was found. Also for long chains, $R_i\{CCl_2O\}/R_i\{C_2Cl_4O\} = 2k_{95a}/k_{95} = 1.3$ so the branching ratio $k_{95b}/k_{95a} = 0.54$.

The ozonolysis reaction was inhibited by O_2, and in this case the chain termination step was suggested to be as follows:

$$CCl_2OO{\cdot}C_2Cl_4 + O_2 \rightarrow CCl_2OO{\cdot}C_2Cl_4{\cdot}O_2 \qquad (97)$$

$$CCl_2OO{\cdot}C_2Cl_4{\cdot}O_2 + C_2Cl_4 \rightarrow 3CCl_2O + C_2Cl_4O \qquad (98)$$

The rate law for high pressures of oxygen then becomes

$$R_i\{CCl_2O\} = 4k_{92}[O_3][C_2Cl_4] \qquad (XXII)$$

where the upper limit of k_{92} was estimated to be $1.2 \times 10^{-2}\ M^{-1}\ s^{-1}$. This second-order rate constant is two orders of magnitude smaller than that obtained by Williamson and Cvetanović for reaction 92 in CCl_4 solution. Since the average value of $k_{92}k_{94}/k_{95}$ from the nitrogen-buffered gas-phase reaction was $0.13\ M^{-1}\ s^{-1}$, the lower limit of the ratio k_{94}/k_{93} becomes about 10.

CH_2CCl_2. The experimental data for the gas-phase ozonolysis of CH_2CCl_2 were more extensive, and Hull et al.[70] proposed the following chain mechanism:

$$CH_2CCl_2 + O_3 \rightarrow CH_2O + CCl_2OO \qquad (99a)$$

$$\rightarrow CH_2OO + CCl_2O \qquad (99b)$$

$$CCl_2OO + O_3 \rightarrow CCl_2O + 2O_2 \qquad (93)$$

$$CCl_2OO + CH_2CCl \rightarrow CCl_2OO{\cdot}CH_2CCl_2 \qquad (100)$$

TABLE XIII. Elementary Rate Constants in the Mechanism of Ozonolysis of 1,1-Dichloroethylene at 25 °C[a]

Rate constant	Value	Units
$k_{99a}k_{101}/k_{103}$	2.4×10^6	$M^{-2}\,s^{-1}$
k_{101a}/k_{101}	0.6	None
k_{101b}/k_{101}	0.4	None
$k_{93}k_{101}/k_{93}k_{103}$	$\sim 1.9 \times 10^5$	M^{-1}
k_{99a}	1.1	$M^{-1}\,s^{-1}$
k_{102a}/k_{102b}	4	None
k_{101}/k_{103}	2.1×10^6	M^{-1}

[a] From Hull et al.[70]

$$CCl_2OO{\cdot}CH_2CCl_2 + O_3 \rightarrow CCl_2OO{\cdot}CH_2CCl_2{\cdot}O_3 \qquad (101a)$$

$$\rightarrow CCl_2OO + CCl_2O + HCOOH \qquad (101b)$$

$$CCl_2OO{\cdot}CH_2CCl_2 + O_2 \rightarrow CCl_2OO{\cdot}CH_2CCl_2{\cdot}O_2 \qquad (102a)$$

$$\rightarrow 2CCl_2O + HCOOH \qquad (102b)$$

$$CCl_2OO{\cdot}CH_2CCl_2 \rightarrow CCl_2O + CH_2CCl_2O \qquad (103)$$

$$CH_2O + O_3 \rightarrow O_2 + HCOOH \text{ (or } CO + H_2O) \qquad (104)$$

$$CCl_2OO{\cdot}CH_2CCl_2{\cdot}O_3 + 2CH_2CCl_2 \rightarrow 3CH_2CCl_2O + CCl_2OO \qquad (105)$$

$$CCl_2OO{\cdot}CH_2CCl_2{\cdot}O_2 + CH_2CCl_2 \rightarrow 2CH_2CCl_2O + CCl_2OO \qquad (106)$$

The Criegee dissociation of the initial ozone–olefin adduct can occur in two ways, but on the basis of the reaction products, the stoichiometry, and the dependence of the rates on oxygen, Hull et al. proposed that reaction 99a was the dominant primary step. Following this step, the propagation of the chain reaction is maintained by CCl_2OO through reactions 100, 101, 105, and 106. Reaction 104 was included to account for the absence of CH_2O among the products. The product CH_2CCl_2O in steps 103, 105, and 106 was considered to be vibrationally excited and to be the source of the rearranged acid chloride $CH_2ClCCl(O)$ and the products HCl and CO. In the absence of O_2 and for long chains, if $k_{103} \ll k_{101}[O_3]$, the above mechanism gives

$$-d[O_3]/dt = 2k_{99a}[CH_2CCl_2][O_3] + \frac{k_{99a}[CH_2CCl_2][O_3](k_{93}[O_3] + k_{100}[CH_2CCl_2])}{k_{93}[O_3] + k_{100}k_{103}[CH_2CCl_2]/k_{101}[O_3]} \qquad (XXIII)$$

At high CH_2CCl_2 but low O_3 pressures, eq XXIII reduces to

$$-d[O_3]/dt = (k_{99a}k_{101}/k_{103})[CH_2CCl_2][O_3]^2 \qquad (XXIV)$$

while at high O_3 but low CH_2CCl_2 pressures it becomes

$$-d[O_3]/dt = (k_{99a}k_{100}/k_{93})[CH_2CCl_2]^2 \qquad (XXV)$$

since under all the experimental conditions $k_{93}[O_3] \ll k_{100}[CH_2CCl_2]$. The latter rate equation was proposed as the reason for the faster rates observed initially in both N_2 and O_2 buffered reactions (see Figures 1 and 2 in ref 70). For all pressure conditions, moreover, the mechanism gives:

$$d[CH_2CCl_2]/d[O_3] = 1 + 2k_{101a}/k_{101} \qquad (XXVI)$$

and

$$-d[CCl_2O]/d[O_3] = k_{101b}/k_{101} \qquad (XXVII)$$

When O_2 is present in excess and $(k_{101b}k_{100}/k_{102})[CH_2CCl_2] \gg k_{93}[O_3]$, the predicted rates are

$$d[CCl_2O]/dt = -d[O_3]/dt = 2k_{99a}[CH_2CCl_2][O_3] \qquad (XXVIII)$$

and the consumption ratio of the reactants becomes

$$d[CH_2CCl_2]/d[O_3] = 1 + k_{102a}/k_{102b} \qquad (XXIX)$$

TABLE XIV. Elementary Rate Constants in the Mechanism of Ozonolysis of 1,2-Dichloroethylene at 23 °C[a]

Rate constant	Cis isomer	Trans isomer	Units
k_{107}	22	148	$M^{-1}\,s^{-1}$
k_{108}/k_{-107}	4.6×10^4	4.6×10^4	M^{-1}
k_{109}/k_{-107}	3.2×10^4	3.2×10^4	M^{-1}
k_{111a}/k_{111b}	3.0	1.0	None
k_{112}/k_{111}	~2	~2	None

[a] From Blume et al.[71]

Comparison of the derived rate equations and various ratios of the rates with those determined experimentally permitted Hull et al. to evaluate the elementary rate constants given in Table XIII. In the study of Williamson and Cvetanović,[69] the olefin concentrations, which were always in excess over the ozone concentration in the CCl_4 solutions, were equivalent to 2–92 Torr range, and thus similar to the pressure range used by Hull et al. in N_2-buffered gas-phase studies. Therefore, if the rate observed by Williamson and Cvetanović corresponds to that of reaction 99a, then this reaction is 20 times faster in CCl_4 solution than in the N_2 buffered gas phase.

CHClCHCl. The unusual changes in reaction order with pressure, the isomerization of the reactant, and the inhibition of the rate by O_2 suggested to Blume et al.[71] that the mechanism of the ozonolysis of *cis*- or *trans*-dichloroethylene (DCE) was a very complex chain reaction. The simplest mechanism which accounted for the observed results except the isomerization was proposed to be as follows:

$$R_2 + O_3 \rightleftarrows R_2O_3 \tag{107}$$

$$R_2O_3 + R_2 \rightleftarrows R_4O_3 \tag{108}$$

$$R_4O_3 + O_3 \rightarrow 2RO + 2RO_2 \tag{109}$$

$$RO_2 + R_2 \rightleftarrows R_3O_2 \tag{110}$$

$$R_3O_2 + O_3 \rightarrow R_3O_5 \xrightarrow{R_2,O_3} 4RO + RO_2 + O_2 \tag{111a}$$

$$\rightarrow 3RO + O_2 \tag{111b}$$

$$R_3O_2 + O_2 \rightarrow R_3O_4 \xrightarrow{O_3} 3RO + 2O_2 \tag{112}$$

Here, DCE is represented by R_2, and RO_2 (the Criegee diradical) is the chain carrier. Reactions 111b and 112 are the chain termination steps, but whichever step is operating the overall stoichiometry becomes the same as that observed experimentally. Steady-state approximations for the various reaction intermediates allow the derivation of the following rate equations.

$$R\{109\} = \frac{k_{107}k_{108}k_{109}[R_2]^2[O_3]^2}{k_{108}k_{109}[R_2][O_3] + k_{-107}(k_{-108} + k_{109}[O_3])} \tag{XXX}$$

$$d[RO]/dt = 2R\{109\} \times \left\{1 + \frac{(4k_{111a} + 3k_{111b})[O_3] + 3k_{112}[O_2]}{k_{111b}[O_3] + k_{112}[O_2]}\right\} \tag{XXXI}$$

The rate of disappearance of ozone, $-R\{O_3\}$, or of the olefin, $-R\{R_2\}$, is given by one-half the right-hand side of eq XXXI, and the expression enclosed in braces provides the O_2 dependence of the rate. With no O_2, this expression reduces to $\{4 + 4(k_{111a}/k_{111b})\}$ while with excess O_2 it becomes simply $\{4\}$. The $R\{109\}$ coefficient in eq XXXI, on the other hand, reduces to different expressions depending on the pressures of the reactants. For low R_2 and O_3 pressures

$$R\{109\} = \frac{k_{107}k_{108}k_{109}}{k_{-107}k_{-108}}[R_2]^2[O_3]^2 \tag{XXXII}$$

so the reaction rate becomes fourth order overall. If $[R_2]$ is high, then

$$R\{109\} = k_{107}[R_2][O_3] \tag{XXXIII}$$

Finally, when $[O_3]$ is high, the $R\{109\}$ term reduces to

$$R\{109\} = (k_{107}k_{108}/k_{-107})[R_2]^2[O_3] \tag{XXXIV}$$

The three rate laws XXXII–XXXIV correspond to the three limiting cases observed experimentally.

By a computer fit of all the data, the pertinent ratios of rate coefficients for the mechanism consisting of reactions 107–112 were obtained, and they are summarized in Table XIV. If the second-order rate constants determined from the CCl_4 solution by Williamson and Cvetanović[69] were the same as k_{107}, then the gas-phase constants for *cis*- and *trans*-DCE are, respectively, about 0.62 and 0.25 of those in CCl_4 solution. In CCl_4 solution, the trans isomer reacted 17 times faster than did the *cis*-DCE, while in the gas phase the trans isomer reacted only 6.7 times faster in the second-order limit. In comparison to these differences, Carles and Fliszár[105] found that the ozonolysis of *trans*-2-pentene was just 1.5 times faster than the cis isomer reaction in CCl_4 solution at 0 °C.

The mechanism proposed here also provides possible channels for the isomerization of the DCE which was observed during the ozonolysis reaction. If the products of reactions 107, 108, and/or 109 are noncyclic with loss of carbon–carbon double bond character, then their decompositions to the reactants will give an isomer different from the initial reactants. Unfortunately, the ozonolysis rates of *cis*- and *trans*-DCE were too similar in the gas phase and the experimental data were not sufficient to make any quantitative deductions concerning this isomerization reaction. However, it appears that channels −107, −108, and −110 are not sufficient to explain the isomerization results, and other channels are needed.

C. Discussion

Although the available information, both experimental and mechanistic, on each haloethylene reviewed here is not sufficient to derive a complete general mechanism for the ozonolysis of simple olefins, two significant characteristics of such reactions emerge when the entire data are examined together. First, many of these ozonolysis reactions are inhibited by molecular oxygen. Such inhibitions have been observed in the ozonolysis of C_2Cl_4,[5] CH_2CCl_2,[70] *cis*- and *trans*-CHClCHCl,[71] and CH_2CHCl.[94] This inhibition has been reported now even for CH_2CH_2.[73,83] Oxygen inhibition was not reported in the ozonolysis of C_2F_4,[68] but in this case the oxygen is a reaction product and the $[O_3]_0 > [C_2F_4]$ condition used in the gas-phase study would have made it difficult to observe this inhibition, since molecular O_2 was not added deliberately. Thus, it appears that oxygen inhibition may be a general characteristic of the haloethylene ozonolysis reactions, and it may be so even in the ozonolysis of other simple olefins. The mechanisms of these reactions, therefore, presumably are of a free radical type, each involving a biradical species.

The second significant characteristic of the ozonolysis reactions reviewed here concerns the origin of the biradical species which caused the oxygen inhibition described above. In the low-temperature infrared study of the ozonolysis of CH_2CH_2,[88] both the primary and secondary ozonides were detected. Thus, the reaction in this case may be considered to proceed by the Criegee-type mechanism where the primary ozonide is the source of the biradical species. The infrared study of the low-temperature ozonolysis of CH_2CCl_2 and CHClCHCl,[92] on the other hand, showed no formation of primary ozonides even though the reactions were taking place as evidenced by the appearance of the infrared bands of phosgene and formyl chloride, respectively. The source of the biradicals for these reactions, therefore, appears to be other than the primary ozonides. Detailed kinetic studies, as will be discussed, also appear to argue against the primary ozonide intermediate. In the case of the low-temperature ozonolysis of CH_2CHCl,[92] the formation of both formyl chloride and the primary ozonide was observed in a temperature range where the decomposition rate of the latter was negligible. Thus, two independent reaction paths appear to be available here, one involving the primary ozonide and the other channel by-passing this intermediate. These spectroscopic observations indicate, in fact, that the parallel path reaction mechanism proposed by Williamson and Cvetanović[69] consisting of reaction steps 89–91 may be correct in principle, and, furthermore, it can now be modified to be consistent with the experimental observations.

For a general olefin RR′ the Criegee path of biradical formation is given by Scheme I. Reaction 113 is irreversible and leads to the primary ozonide which provides the biradical RO_2, and $R'O_2$ in case of an unsymmetrical olefin. In addition the trioxolane opens and decomposes to other mono-free-radical and molecular products as proposed by O'Neal and Blumstein.[97] The second reaction channel, which we shall call the π-complex path of biradical formation (Scheme II), is based primarily on the requirements provided by the kinetic study of *cis*- and *trans*-CHClCHCl. This scheme consists of two reversible reactions 107′ and 108′ followed by an irreversible step 109′. The products of reaction 107′ may be the π complexes which have been observed with many olefins at low temperatures.[88,92] According to the low-temperature studies with *cis*- or *trans*-CHClCHCl, the reverse of reaction 107′ does not involve an isomerization, but the reverse of reaction 108′ may.[92] Both the π-complex and Criegee paths may be important in the ozonolysis of CH_2CHCl, but for the other chloroethylenes only the π complex appears necessary to account for the experimental observations.

SCHEME I. Criegee Path

$$RR' + O_3 \rightarrow \overline{RR'OOO} \qquad (113)$$

$$\overline{RR'OOO} \rightarrow RO_2 + R'O \qquad (114a)$$

$$\rightarrow R'O_2 + RO \qquad (114b)$$

$$\overline{RR'OOO} \rightarrow \text{other products} \qquad (115)$$

SCHEME II. π-Complex Path

$$RR' + O_3 \rightleftarrows RR'O_3 \qquad (107')$$

$$RR'O_3 + RR' \rightleftarrows R_2R_2'O_3 \qquad (108')$$

$$R_2R_2'O_3 + O_3 \rightarrow 2R'O + 2RO_2 \qquad (109a')$$

$$\rightarrow 2RO + 2R'O_2 \qquad (109b')$$

Thus we see that the O_3 reactions proceed primarily by different paths for different ethylenes, similar to the observation for O-atom reactions. Earlier in this review we showed that there are three classes of O-atom reactions, one for C_2H_4 and CH_2CHCl, one for the fluoroethylenes except CF_2CCl_2, and one for the other chloroethylenes including CF_2CCl_2.

Likewise we find here that C_2H_4 and CH_2CHCl (and the higher unhalogenated olefins) form molozonides which decompose by the Criegee mechanism to give a rate law first order in both olefin and O_3 over the entire pressure range. On the other hand, the higher chloroethylenes do not form molozonides and react with O_3 by a complex rate law which deviates from second order (first order in each reactant) at low reactant pressures, indicating reversibility of the initial reaction step. Furthermore CHClCHCl undergoes geometrical isomerization, whereas the 2-butenes do not.

It is not clear from the data whether C_2F_4 ozonolysis fits into one of these reaction classes or proceeds by a third scheme, as in O-atom attack on C_2F_4. No deviation was observed in the second-order rate law over the range studied, but, by analogy with C_4F_8-2 which did show the deviation, Heicklen[68] interpreted his data in terms of a changing rate law. However, Heicklen believed that no CF_2O_2 diradicals were present because no tetrafluoroethylene oxide was observed as a product in the room-temperature gas-phase ozonolysis, yet it was a product when CF_2O_2 was produced in the C_2F_4–O_2–O system.[46,67] If Heicklen's inference is correct, then the ozonolysis of C_2F_4 must be different from that for either the olefins or the chloroethylenes. One note of caution in this inference is that CF_2OO may exist as either a triplet or singlet species, which may react differently. Thus the triplet CF_2OO (presumably produced in the O–O_2–C_2F_4 system) might lead to tetrafluoroethylene oxide whereas the singlet CF_2OO (as expected in the O_3–C_2F_4 system) might not lead to this product. However, if CF_2OO is not produced, the π-complex mechanism might still explain the results by adding the reaction

$$R_2R_2'O_3 + O_3 \rightarrow 2RO + 2R'O + O_2 \qquad (109c')$$

Once the diradical RO_2 (or $R'O_2$) is produced, it can participate in a chain process, an example of which is given by reactions in Scheme III.

SCHEME III. Chain Propagation and Termination

$$RO_2 + RR' \rightarrow R_2R'O_2 \qquad (110')$$

$$RO_2 + O_3 \rightarrow RO + 2O_2 \qquad (116)$$

$$R_2R'O_2 \rightarrow RO + RR'O \qquad (117)$$

$$R_2R'O_2 + O_3 \rightarrow R_2R'O_5 \qquad (111a')$$

$$\rightarrow 2RO + R'O + O_2 \qquad (111b')$$

$$R_2R'O_5 + RR' \rightarrow R_3R_2'O_5 \qquad (118a)$$

$$\rightarrow RR'O + RO + R'O + RO_2 \qquad (118b)$$

$$R_3R_2'O_5 + O_3 \rightarrow 2RO + 2R'O + O_2 + RO_2 \qquad (119)$$

Here, RO and R′O are the carbonyl products while RR′O may be an epoxide or a rearranged product such as an acid chloride. The biradical chain carrier is RO_2 but the oxygen inhibition of the rate is represented by the reactions in Scheme IV.

SCHEME IV. Oxygen Inhibition

$$R_2R'O_2 + O_2 \rightarrow R_2R'O_4 \qquad (112')$$

$$R_2R'O_4 + O_3 \rightarrow 2RO + R'O + 2O_2 \qquad (120)$$

$$R_2R'O_4 + RR' \rightarrow RR'O + 2RO + R'O \qquad (121)$$

For the chloroethylenes, the mechanism consisting of reactions 107′, 108′, 109a′, 109b′, 110′, 116, 117, 111a′, 111b′, and 112′ leads to the generalized rate law

$$\frac{-d[RR']}{dt} = \left(\frac{2\alpha k_{107'}k_{108'}[O_3][RR']^2}{k_{-107'} + k_{108'}\alpha[RR']}\right) \times \left(1 + \frac{k_{110'}[RR']}{\beta k_{110'}[RR'] + k_{116}[O_2]}\right) \qquad (XXXV)$$

except for stoichiometric factors which depend on the fates of $R_2R'O_5$ (reactions 118 and 119) and $R_2R'O_4$ (reactions 120 and 121). In eq XXXV, the quantities α and β are defined by

$$\alpha \equiv (k_{109a'} + k_{109b'})[O_3]/(k_{-108'} + (k_{109a'} + k_{109b'})[O_3])$$

$$1 - \beta \equiv k_{111a'}[O_3]/(k_{111'}[O_3] + k_{112'}[O_2] + k_{117})$$

The rate law, eq XXXV, is adequate to give calculated rate equations which are consistent with the experimental equations. For example, the gas-phase ozonolysis of C_2F_4 can be interpreted on the basis of the π-complex path. Since the reaction products were O_2 and CF_2O, reaction 109c′ can replace reactions 109a′ and 109b′ to obtain for the rate of formation of CF_2O

$$R\{CF_2O\} = \frac{4k_{107'}k_{108'}[O_3][C_2F_4]^2}{k_{-107'} + k_{108'}[C_2F_4]} \qquad (XXXVI)$$

which is independent of oxygen pressure. In the case of C_2Cl_4, assuming long chains with k_{117} and $k_{111b'}$ considered small compared to $k_{111a'}$, the rate laws in the absence of O_2 become

$$R_i\{CCl_2O\} = \frac{k_{107'}k_{110'}}{k_{116}}\left(1 + \frac{k_{118a}}{k_{118}}\right)[C_2Cl_4]^2 \qquad \text{(XXXVII)}$$

$$R_i\{C_2Cl_4O\} = \frac{2k_{107'}k_{110'}k_{118b}}{k_{116}k_{118}}[C_2Cl_4]^2 \qquad \text{(XXXVIII)}$$

where C_2Cl_4O includes both $\overline{CCl_2CCl_2O}$ and $CCl_3CCl(O)$, and in the presence of O_2

$$R_i\{CCl_2O\} = 8k_{107'}[C_2Cl_4][O_3] \qquad \text{(XXXIX)}$$

Similarly, a long-chain process for the ozonolysis of CHClCHCl gives

$$-d[O_3]/dt = -d[CHClCHCl]/dt = d[HCClO]/2dt$$
$$= \frac{4k_{107'}k_{108'}k_{109'}[CHClCHCl]^2[O_3]^2}{k_{-107'}(k_{-108'} + k_{109'}[O_3]) + k_{108'}k_{109'}[CHClCHCl][O_3]} \times \left\{\frac{k_{111'}[O_3] + k_{112'}[O_2]}{k_{111b'}[O_3] + k_{112'}[O_2]}\right\} \qquad \text{(XL)}$$

where in eq XL reaction 109c′ is assumed to be negligible.

For the unsymmetrical olefin CH_2CCl_2 the chain carrier was deduced to be CCl_2OO rather than CH_2OO. Furthermore, no formaldehyde was observed as a product of the ozonolysis, so the reaction

$$R'O + O_3 \rightarrow HCOOH \text{ (or } CO + H_2O) + O_2 \qquad (122)$$

must be included in the general mechanism. The use of steady-state approximations on the various intermediates including R′O and the assumption of long chains lead to the following rate equations.

$$\frac{-d[O_3]}{dt} = \frac{2k_{107'}[CH_2CCl_2][O_3]}{k_{117} + k_{112'}[O_2]} \times \left\{2k_{111a'}[O_3]\left(1 + \frac{k_{118a}}{k_{118}}\right) + 3k_{112'}[O_2]\right\} \qquad \text{(XLI)}$$

$$\frac{-d[CH_2CCl_2]}{dt} = \frac{2k_{107'}[CH_2CCl_2][O_3]}{k_{117} + k_{112'}[O_2]} \times \{2k_{111a'}[O_3] + 3k_{112'}[O_2]\} \qquad \text{(XLII)}$$

$$\frac{d[CCl_2O]}{dt} = \frac{2k_{107'}[CH_2CCl_2][O_3]}{k_{117} + k_{112'}[O_2]} \times \left\{\frac{k_{111a'}k_{118b}}{k_{118}}[O_3] + k_{112'}[O_2]\right\} \qquad \text{(XLIII)}$$

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VII. References

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