# THE Hg 6($^3$P)-SENSITIZED PHOTO-OXIDATION OF $C_2Cl_3H$

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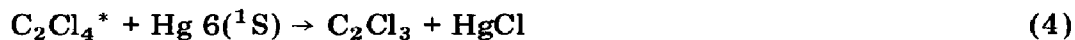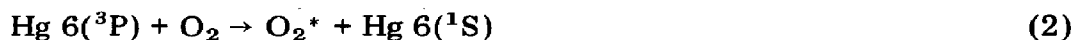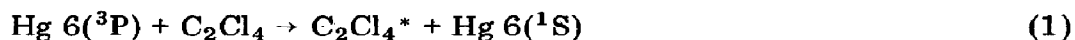
## Summary

The Hg 6($^3$P)-sensitized photolysis of $C_2Cl_3H$ was studied at 25 °C both in the absence and presence of $O_2$. For $C_2Cl_3H$ alone, the main products are $Hg_2Cl_2$ and a solid deposit. Small amounts of an unidentified product with infra-red bands at 720 and 770 $cm^{-1}$ were also found.
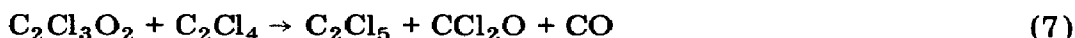
In the presence of $O_2$ the major products are $CCl_2HCCl(O)$, CO, $CCl_2O$, and HCl. These products are produced in a long chain free radical process. Quantitative analysis was not done for HCl, but for the other products and for $C_2Cl_3H$ disappearance, the quantum yields were independent of $I_a$ and $[O_2]$, unless $[O_2]/[C_2Cl_3H] > 4$ in which case the yields dropped as the ratio increased. For $[O_2]/[C_2Cl_3H] < 4$, the quantum yields were related to $[C_2Cl_3H]$ *via* the expressions: $-\Phi\{C_2Cl_3H\} = 5.0[C_2Cl_3H]$, $\Phi\{CCl_2HCCl(O)\} = 4.0[C_2Cl_3H]$, $\Phi\{CO\} - 1 = 0.64[C_2Cl_3H]$, and $\Phi\{CCl_2O\} = 0.14[C_2Cl_3H]$, where the olefin pressure is in Torr. A detailed mechanism, based on the chlorine atom chain oxidation, is presented, and appropriate rate constant ratios are evaluated. It is concluded that Hg 6($^3$P) sensitization of $C_2Cl_3H$ leads to monoradical production.

## Introduction

In an earlier study [1] of the Hg-sensitized oxidation of $C_2Cl_4$ we found that a long chain oxidation occurred similar to that in the chlorine atom initiated oxidation. The chain length was proportional fo $[C_2Cl_4]$, but independent of $[O_2]$ or the absorbed intensity, $I_a$. The results could be explained by the mechanism:

$$Hg\ 6(^3P) + C_2Cl_4 \rightarrow C_2Cl_4{}^* + Hg\ 6(^1S) \tag{1}$$

$$Hg\ 6(^3P) + O_2 \rightarrow O_2{}^* + Hg\ 6(^1S) \tag{2}$$

$$O_2{}^* + C_2Cl_4 \rightarrow C_2Cl_4{}^* + O_2 \tag{3}$$

$$C_2Cl_4{}^* + Hg\ 6(^1S) \rightarrow C_2Cl_3 + HgCl \tag{4}$$

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$$C_2Cl_3 + O_2 \rightarrow C_2Cl_3O_2 \tag{5}$$

$$C_2Cl_3O_2 \rightarrow CO \text{ } via \text{ termination} \tag{6}$$
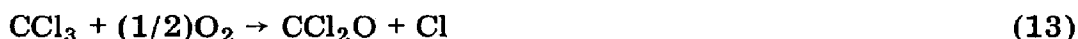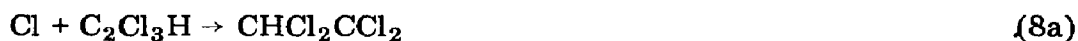
$$C_2Cl_3O_2 + C_2Cl_4 \rightarrow C_2Cl_5 + CCl_2O + CO \tag{7}$$

followed by the chain oxidation of $C_2Cl_5$. In the above mechanism the asterisk superscript denotes electronic excitation. Reaction (6) is an unusual reaction. It may occur on the wall and must ultimately involve another radical. It must be kinetically first-order in radicals, because the chain length is independent of the absorbed intensity, $I_a$. CO is presumably a product of this reaction since $\Phi\{CO\} = 1.0$, and CO is not produced in the chain steps.

The free-radical oxidation of $C_2Cl_3H$ has also been studied [2 - 4], and the mechanism has been shown to be:

$$Cl + C_2Cl_3H \rightarrow CHCl_2CCl_2 \tag{8a}$$

$$\rightarrow CCl_3CHCl \tag{8b}$$

$$R + O_2 \rightarrow RO_2 \tag{9}$$

$$2RO_2 \rightarrow (RO)_2 + O_2 \tag{10a}$$

$$\rightarrow 2RO + O_2 \tag{10b}$$

$$CHCl_2CCl_2O \rightarrow CHCl_2CCl(O) + Cl \tag{11}$$

$$CCl_3CHClO \rightarrow CO + HCl + CCl_3 \tag{12}$$

$$CCl_3 + (1/2)O_2 \rightarrow CCl_2O + Cl \tag{13}$$

where R is either $CHCl_2CCl_2$ or $CCl_3CHCl$.

In this paper we extend our previous studies and report on the Hg-sensitized photo-oxidation of $C_2Cl_3H$. The purpose of this work was to establish the initial fragmentation step in the Hg sensitization. There are three possibilities. First is the possibility of molecular elimination as occurs in $C_2H_4$ and $C_2H_3F$:

$$Hg \text{ } 6(^3P) + C_2Cl_3H \rightarrow Hg \text{ } 6(^1S) + C_2Cl_2 + HCl \tag{14}$$
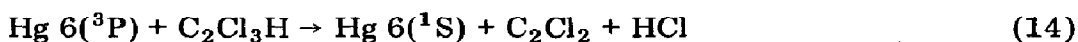
Second is the possibility of double-bond cleavage as occurs in $C_2F_4$:

$$Hg \text{ } 6(^3P) + C_2Cl_3H \rightarrow Hg \text{ } 6(^1S) + CCl_2 + CClH \tag{15}$$

and finally is the possibility of mono-radical formation as occurs in $C_2Cl_4$:

$$Hg \text{ } 6(^3P) + C_2Cl_3H \rightarrow HgCl + C_2Cl_2H \tag{16}$$

Reaction (14) leads to no chain oxidation since free radicals are not produced. Both reactions (15) and (16) should lead to the free radical oxidation, but the rate laws would be different. If reaction (15) occurred the system should behave identically to the $O(^3P)$-atom initiated oxidation and the chain length would depend on $[C_2Cl_3H]/I_a^{1/2}$ [4]. Finally, if reaction (16) occurred, the free radical oxidation should behave analogously to that for the Hg-sensitized oxidation of $C_2Cl_4$, $i.e.$ there should be no intensity dependence.

Our results show a long-chain oxidation with a rate law independent of intensity, and reaction (16) must be operative. Reaction (16) may not be a one-step process, and may proceed through an excited $C_2Cl_3H$ intermediate. In fact our detailed observations suggest that this is the case, as will be discussed later.

## Experimental

The experimental procedure was identical to the infrared technique described previously [4]. The gases were irradiated in a T-shaped reaction vessel with the top of the T situated in a Beckman IR-10 spectrophotometer. The top of the T was 12.0 cm in length except for a few runs in which a cell of 6.7 cm length was used.

Since $O_3$ was produced during the reaction, and it inhibited the reaction, the irradiation was periodically interrupted and the reaction vessel shaken, so that the Hg drop would react with the $O_3$. For each run a new Hg drop was used.

For a number of experiments the reaction mixture was irradiated in a quartz cell. At the end of the series, the cell was rinsed with dilute $HNO_3$. $AgNO_3$ was added to the resultant solution, and the characteristic AgCl precipitate was obtained.

## Results

In the Hg-sensitized photolysis of $C_2Cl_3H$ at 25 °C in the absence of $O_2$, the major product is a solid deposit. The Hg drop becomes coated and, when dissolved in $HNO_3$ and reacted with $AgNO_3$, gives a AgCl precipitate indicating the presence of $Hg_2Cl_2$. The only other product found was condensable at $-90$ °C and had infra-red absorption bands at 770 and 720 $cm^{-1}$, the former being more intense. We were unable to identify this product, and refer to it as product X.

The loss of $C_2Cl_3H$ was monitored and the quantum yields of consumption, $-\Phi\{C_2Cl_3H\}$, are shown in Table 1. The results are somewhat scattered, $-\Phi\{C_2Cl_3H\}$ being $< 1.0$ at the highest intensities and 1.5 - 2.0 at lower intensities. However, there is no pressure effect, and it is clear that a long chain polymerization is not involved. As a first approximation, $-\Phi\{C_2Cl_3H\} \sim 1.0$. Also shown is an attempted analysis for the unknown product X, based on the assumption that its infra-red bands have extinction coefficients similar to the average of the C—Cl stretch for $C_2Cl_4$, $C_2Cl_3H$, and $C_2H_2Cl_2$ in the 700 - 800 $cm^{-1}$ region. It can be seen that X is a minor product.

In the presence of $O_2$, the Hg drop became coated, but the coating was different than in the absence of $O_2$. While some $Hg_2Cl_2$ may be present, presumably most of the coating is HgO. The major gaseous product was $CCl_2HCCl(O)$ with smaller amounts of CO and $CCl_2O$. We were unable to determine the absence or presence of $C_2Cl_4$ or $CCl_3H$ because their vapor

**TABLE 1**

Hg-sensitized photolysis of $C_2Cl_3H$ at 25 °C

| $[C_2Cl_3H]$ (Torr) | $I_a$ (mTorr/s)[a] | $-\Phi\{C_2Cl_3H\}$ [b] | $\dfrac{[X]}{\Delta[C_2Cl_3H]}$ [c] |
|---|---|---|---|
| 0.65 | 0.94 | 0.80 | <0.07 |
| 1.46 | 0.29 | 1.8 | <0.08 |
| 1.56 | 0.91 | 0.68 | — |
| 2.54 | 0.16 | 1.53 | — |
| 4.72 | 0.33 | 2.00 | — |

[a] $I_a$ at the beginning of the run.  [b] From the initial decay rate.
[c] The amount of the unidentified product produced per $C_2Cl_3H$ consumed for long exposure.

pressures are similar to and their infra-red spectra underlie those of $C_2Cl_3H$ and $CCl_2HCCl(O)$. However, both CHClCHCl and $CCl_3CH(O)$ were absent, the quantum yield of the latter being < 0.01 $\Phi\{CCl_2HCCl(O)\}$. We reported in our previous work [4] that HCl was not found, but this represents a lack of sensitivity. In this study we also could not detect HCl in any individual experiment. However, if the fraction of the reacted mixtures non-condensable at −130 °C from several runs was collected, then the characteristic infra-red bands of HCl at 2750 - 3050 cm$^{-1}$ could be detected.

Figure 1 shows a first-order decay plot for $C_2Cl_3H$ in the Hg-sensitized photo-oxidation of $C_2Cl_3H$. If the irradiations are periodically interrupted, and the reaction cell shaken, then good first-order plots are obtained. The slope of the line gives the decay coefficient for $-\Phi\{C_2Cl_3H\}$ = 4.7$[C_2Cl_3H]$ where $[C_2Cl_3H]$ is expressed in Torr. This expression holds for runs in which the initial $C_2Cl_3H$ pressure, $[C_2Cl_3H]_0$, was varied by a factor of 4.9; $[O_2]$, by a factor of 6.7; and $I_a$, by a factor of 2.2. One set of data points shows a marked inhibition. In this run the reaction cell was not shaken periodically. We take this as evidence for $O_3$ accumulation, since $O_3$ inhibits the free radical oxidation of $C_2Cl_4$ [5]. Shaking the reaction cell removes the $O_3$ by reaction with the Hg drop to produce HgO which coats the drop.

Product quantum yields in the oxidation are listed in Table 2. The reaction parameters were varied by the following factors: $[C_2Cl_3H]_0$, 16.2; $[O_2]$, 157; $I_a$, 10. The quantum yields all increase with $[C_2Cl_3H]$, are independent of $I_a$, and are independent of $[O_2]$ until $[O_2]/[C_2Cl_3H]$ > 4. Then the quantum yields drop slowly as $[O_2]/[C_2Cl_3H]$ is further raised. Even for $[O_2]/[C_2Cl_3H]$ < 4, $\Phi\{CO\}$ and $\Phi\{CCl_2O\}$ are lower if the cell was not shaken continually during the run. We consider this further evidence for inhibition due to $O_3$ formation. For those runs with $[O_2]/[C_2Cl_3H] \leqslant 4$, the dependence of the quantum yields on $[C_2Cl_3H]$ is shown graphically in Fig. 2. (In those runs in which the cell was not shaken continually, the data points for $\Phi\{CO\}$ and $\Phi\{CCl_2O\}$ are omitted from the graphs.) For $-\Phi\{C_2Cl_3H\}$ and $\Phi\{CCl_2HCCl(O)\}$, the plots give good straight lines of
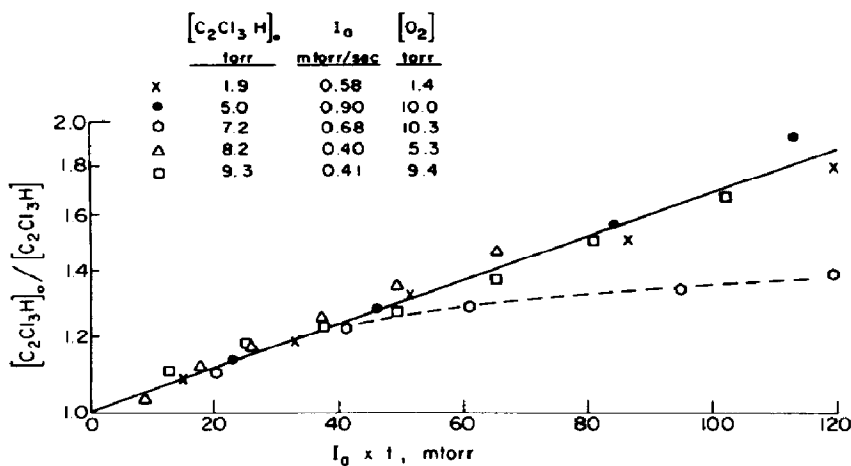
| | $[C_2Cl_3H]_o$ | $I_a$ | $[O_2]$ |
|---|---|---|---|
| | torr | mtorr/sec | torr |
| x | 1.9 | 0.58 | 1.4 |
| ● | 5.0 | 0.90 | 10.0 |
| ○ | 7.2 | 0.68 | 10.3 |
| △ | 8.2 | 0.40 | 5.3 |
| □ | 9.3 | 0.41 | 9.4 |

Fig. 1. Semi-log plot of $[C_2Cl_3H]_o/[C_2Cl_3H]$ $vs.$ $I_a t$ in the Hg-photo-sensitized oxidation of $C_2Cl_3H$ at 25 °C. In each experiment, except those denoted by hexagons, the photolysis was interrupted after every determination and the reaction cell shaken. For the data denoted by hexagons the irradiation was continuous, and the reaction cell was undisturbed during the irradiation.

slope one. For CO, the plot shown is $\Phi\{CO\}$ —1, for reasons to be discussed later. The data for that plot and for $\Phi\{CCl_2O\}$ are badly scattered. We have drawn the straight line of slope one that best fits the data. From the plots, the quantum yields are seen to be proportional to $[C_2Cl_3H]$. The proportionality constants are 5.0, 4.0, 0.64, and 0.14 $Torr^{-1}$, respectively, for $-\Phi\{C_2Cl_3H\}$, $\Phi\{CCl_2HCCl(O)\}$, $\Phi\{CO\}$ — 1, and $\Phi\{CCl_2O\}$. The value of 5.0 $Torr^{-1}$ for $-\Phi\{C_2Cl_3H\}$ is in good agreement with the value of 4.7 $Torr^{-1}$ found from Fig. 1.

One run was done in which the Hg-sensitized photo-oxidation of $CCl_2$-$HCCl(O)$ was studied. The reaction parameters were: $[CCl_2HCCl(O)]$ = 1.75 Torr, $[O_2]$ = 3.70 Torr, and $I_a$ = 0.40 mTorr/s. The results were: $-\Phi\{CCl_2HCCl(O)\}$ ~ 1.0, $\Phi\{CO\}$ ~ 0.5, and $\Phi\{CO\}/\Phi\{CCl_2O\}$ ~ 8.

Discussion

The results of this study are almost exactly analogous to those in the Hg-sensitized oxidation of $C_2Cl_4$ [1]. The oxidation proceeds by a long-chain free radical mechanism, the chain length being proportional to the olefin pressure, but independent of $I_a$ and $[O_2]$. The reaction mechanism is that outlined in the Introduction except that the initiation step (16) is expanded to include excited $C_2Cl_3H$ as an intermediate and all the possible free-radical products:
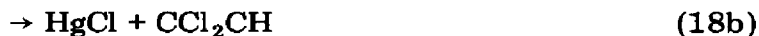
$$Hg\ 6(^3P) + C_2Cl_3H \rightarrow Hg\ 6(^1S) + C_2Cl_3H^* \tag{17}$$

$$C_2Cl_3H^* + Hg\ 6(^1S) \rightarrow Hg\ 6(^1S) + H + C_2Cl_3 \tag{18a}$$

$$\rightarrow HgCl + CCl_2CH \tag{18b}$$

$$\rightarrow HgCl + CClHCCl \tag{18c}$$

TABLE 2

Hg-sensitized photo-oxidation of $C_2Cl_3H$ at 25 °C

| $[C_2Cl_3H]^a$ (Torr) | $[O_2]$ (Torr) | $I_a^b$ (mTorr/s) | Irradiation Time (s) | $-\Phi\{C_2Cl_3H\}^{c,d}$ | $\Phi\{CCl_2HCCl(O)\}^c$ | $\Phi\{CO\}^e$ | $\Phi\{CCl_2O\}^e$ |
|---|---|---|---|---|---|---|---|
| 1.16(0.77) | 9.2 | 0.43 | 280 | 7.0 | 5.0 | 1.14 | — |
| 1.89(1.42) | 1.4 | 0.58 | 200 | 11.0(9.0) | 10.0 | 2.5 | 0.58 |
| 2.48(1.99) | 9.8 | 0.40 | 330 | 11.7 | 8.7 | 1.3 | 0.21 |
| 3.2$^f$ | 10.0 | 0.60 | 600 | 22 | 16 | 0.77$^g$ | — |
| 4.42(3.38) | 5.3 | 0.46 | 200 | 30 | 23 | 3.54 | 0.75 |
| 5.20(4.06) | 5.6 | 0.41 | 250 | 28 | 21 | 4.67 | 0.85 |
| 5.3$^f$ | 7.3 | 0.70 | 340 | 27 | 19 | — | — |
| 5.0(4.4) | 9.8 | 0.09 | 1300 | 19 | 18 | 3.0 | 0.26 |
| 5.0(4.0) | 10.0 | 0.90 | 136 | 28(24) | 22 | 1.86 | 0.45 |
| 5.1(4.0) | 10.2 | 0.42 | 250 | 25 | 24 | 3.9 | 0.49 |
| 5.1(4.3) | 20.7 | 0.40 | 250 | 19 | 17 | 3.0 | 0.41 |
| 5.1(4.5) | 45.0 | 0.40 | 250 | 13.0 | 11.7 | 1.9 | 0.16 |
| 5.2(4.6) | 219 | 0.41 | 345 | 9.9 | 7.8 | 0.9 | 0.11 |
| 7.2$^f$ | 10.3 | 0.68 | 300 | 34 | 33 | 2.0$^g$ | 0.22$^g$ |
| 7.5$^f$ | 10.8 | 0.26 | 1806 | 22 | 21 | 1.1$^g$ | — |
| 8.2(6.9) | 5.3 | 0.49 | 162 | 42(39) | 40 | 8.1 | 1.03 |
| 9.3(7.5) | 9.4 | 0.41 | 250 | 58(44) | 44 | 7.2 | 1.16 |
| 13.8$^f$ | 9.8 | 0.64 | 310 | 60 | 55 | 4.0$^g$ | 0.65$^g$ |
| 18.0(16.5) | 10.3 | 0.40 | 142 | 70 | 60 | 9.9 | 1.65 |

[a] Initial $C_2Cl_3H$ pressures. The values in parentheses are average values for the irradiation. [b] $I_a$ at the beginning of the run. [c] Based on initial rates. [d] Values in parentheses obtained from the slope of Fig. 1. [e] Computed from final values of CO and $CCl_2O$. [f] Top of the reaction T cell was 6.7 rather than 12.0 cm long. [g] The cell was not shaken during the run so that $O_3$ accumulated.
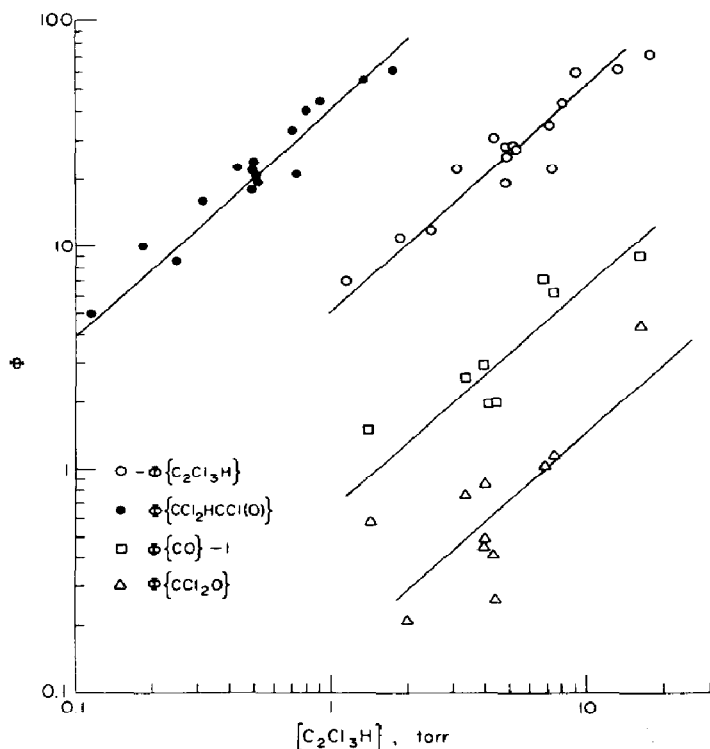
Fig. 2. Log–log plot of the quantum yields *vs.* the $C_2Cl_3H$ pressure in the Hg-sensitized photooxidation of $C_2Cl_3H$ at 25 °C. The initial $C_2Cl_3H$ pressure is used with $-\Phi\{C_2Cl_3H\}$ and $\Phi\{CCl_2HCCl(O)\}$; the average $C_2Cl_3H$ pressure, with $\Phi\{CO\} - 1$ and $\Phi\{CCl_2O\}$. The plot for $\Phi\{CCl_2HCCl(O)\}$ is displaced to the right by a factor of 10 for clarity

If the reaction of Hg $6(^3P)$ with $O_2$ did not lead to oxidation of $C_2Cl_3H$, the chain length would be reduced by half as $[O_2]/[C_2Cl_3H]$ increased from a small value to 2.2, since $k_2/k_{18} = 0.45$ [6]. In fact, there is no noticeable decline in the initial quantum yields until $[O_2]/[C_2Cl_3H] > 4$. Thus reaction (2) is followed by:
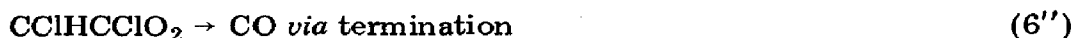
$$O_2{}^* + C_2Cl_3H \to O_2 + C_2Cl_3H^* \tag{19}$$

except at high values of $[O_2]/[C_2Cl_3H]$ where the following reaction can also occur:

$$O_2{}^* + O_2 \to 2O_2 \tag{20a}$$
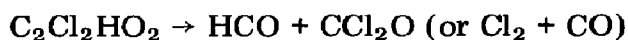$$\to O_3 + O(^3P) \tag{20b}$$

The occurrence of reaction (20) reduces the chain length since the major pathway is reaction (20a) [7]. Reaction (20b) is the source of $O_3$ deduced to be present in our system.

Reactions analogous to reactions (5 - 7) can be written for $CCl_2CH$ and $CClHCCl$ radicals:

$$CCl_2CH + O_2 \rightarrow CCl_2CHO_2 \tag{5'}$$

$$CClHCCl + O_2 \rightarrow CClHCClO_2 \tag{5''}$$

$$CCl_2CHO_2 \rightarrow CO \; via \; termination \tag{6'}$$

$$CClHCClO_2 \rightarrow CO \; via \; termination \tag{6''}$$

$$CCl_2CHO_2 + C_2Cl_3H \rightarrow C_2Cl_4H + HCl + 2CO \tag{7'}$$

$$CClHCClO + C_2Cl_3H \rightarrow C_2Cl_4H + 2CO + HCl \tag{7''}$$

Reactions (6') and (6'') are analogous to reaction (6). Their detailed fate is not known, but a possible sequence of events is:

$$C_2Cl_2HO_2 \rightarrow HCO + CCl_2O \; (or \; Cl_2 + CO)$$

$$HCO + O_2 \rightarrow CO + HO_2$$

$$HO_2 \rightarrow (1/2)H_2O + (1/2)O_2$$

The mechanism leads to the conclusion that if reactions (7), (7'), and (7'') are unimportant compared to reactions (6), (6') and (6'') respectively, then:

$$\Phi\{CO\} - 1 = \Phi\{CCl_2O\} = \Phi\{HCl\} \tag{I}$$

$$-\Phi\{C_2Cl_3H\} = \Phi\{CCl_2HCCl(O)\} + \Phi\{CO\} \tag{II}$$

$$(\Phi\{CO\} - 1)/\Phi\{CCl_2HCCl(O)\} = k_{8b}/k_8 \tag{III}$$

where it is assumed that reactions (6), (6'), and (6'') give one CO and no $CCl_2O$.

The mass balance as given by eqn. (II) is satisfactory, the ratio of the values for the right-hand side of eqn. (II) to those for the left-hand side being 0.93. Our experiments show that $\Phi\{CO\} - 1 = 4.6 \; \Phi\{CCl_2O\}$, a considerable discrepancy from that predicted by eqn. (I). This value is also much higher than 1.7 found for $\Phi\{CO\}/\Phi\{CCl_2O\}$ in the $O(^3P)$-initiated oxidation [4] or 1.85 found for $\Phi\{CO\}/\Phi\{CCl_2O\}$ when a mixture of 15 Torr $Cl_2$, 6.0 Torr $C_2Cl_3H$, and 9.4 Torr $O_2$ was irradiated. Furthermore, the ratio found for $k_{8b}/k_8$ in this study is 0.16, which is measureably higher than the values of 0.10 and 0.066 found in the $O(^3P)$- and Cl-initiated oxidations, respectively. There clearly seems to be an excess production of CO in the Hg-sensitized oxidation.

There are a number of possible paths to give excess CO and reduced $CCl_2O$, but none of them appear to be large enough to account for the discrepancy. For example the $Hg^*$-sensitized oxidation of $CCl_2HCCl(O)$ gives $\Phi\{CO\}/\Phi\{CCl_2O\} \sim 8$. However, $\Phi\{CO\}$ in this reaction is 0.5, so that this is an upper limit to the increment. The Hg-sensitized decomposition of $CCl_2O$, of course, would convert $CCl_2O$ to CO and thus greatly enhance $\Phi\{CO\}/\Phi\{CCl_2O\}$. However, since $\Phi\{CCl_2O\}$ is small, and the deficiency in $CCl_2O$ is not marked, this route again could cause only a small enhancement in $\Phi\{CO\}$. Finally, the presence of $O_3$ could induce reactions that might lead to CO production, but unless there were a chain process, $\Phi\{CO\}$

would not increase markedly. Probably all three sources of excess CO play some role, and possibly the combination of all of them may account for the excess CO.

The mechanism of the reaction leads to the following rate law if reactions (7), (7'), and (7'') are unimportant compared to reactions (6), (6') and (6''), respectively.

$$-\Phi\{C_2Cl_3H\} \; -1 = (k_{10}/k_{10a})\beta[C_2Cl_3H] \tag{IV}$$

where

$$\beta \equiv (k_7k_{18a}/k_6 + k_{7'}k_{18b}/k_{6'} + k_{7''}k_{18c}/k_{6''})/k_{18}$$

Since $-\Phi\{C_2Cl_3H\} \gg 1$, the 1 can be ignored on the left-hand side of eqn. (IV) The proportionality constant of 4.9 Torr$^{-1}$ found from Figs. 1 and 2 can be used to compute $\beta$ since $k_{10}/k_{10a} = 325$ [4]. Thus $\beta = 1.5 \times 10^{-2}$ Torr$^{-1}$. The fraction of the initial photolytic act which leads to chain initiation is $\beta[C_2Cl_3H]$, and this value never exceeds 0.27. Thus the assumption that reactions (7), (7') and (7'') were unimportant compared to reactions (6), (6'), and (6'') is justified.

## Acknowledgement

## References

1 E. Sanhueza and J. Heicklen, Can. J. Chem., 52 (1974) 3863.
2 K. L. Müller and H. J. Schumacher, Z. Phys. Chem., B37 (1937) 365.
3 G. Huybrechts and L. Meyers, Trans. Faraday Soc., 62 (1966) 2191.
4 E. Sanhueza and J. Heicklen, Intern. J. Chem. Kin., 6 (1974) 553.
5 E. Mathias, E. Sanhueza, I.C. Hisatsune and J. Heicklen, Can. J. Chem., 52 (1974) 3852.
6 R. J. Cvetanović, Progr. React. Kinet., 2 (1964) 39.
7 D. H. Volman, J. Chem. Phys., 21 (1953) 2086.