# THE REACTION OF O($^3$P) WITH CCl$_2$CH$_2$
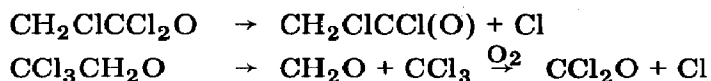
EUGENIO SANHUEZA* and JULIAN HEICKLEN

*Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)*

(Received July 18, 1974)

## Summary

The reaction of O($^3$P), prepared from the Hg photosensitization of N$_2$O, with CCl$_2$CH$_2$ was studied at 25 °C. The products of the reaction in the absence of O$_2$ were CO, CH$_2$ClCCl(O), polymer, and another unidentified compound (as well as N$_2$ from the N$_2$O). The quantum yields of CO and CH$_2$ClCCl(O) were 0.35 ± 0.02 and 0.06 ± 0.01, respectively, independent of reaction conditions. The reaction rate coefficient is identical to that for O($^3$P) + C$_2$F$_4$, *i.e.* 6.0 × 10$^8$ $M^{-1}$ s$^{-1}$.

In the presence of O$_2$ a long free radical chain process occurs in which CH$_2$ClCCl(O) is the major product and CCl$_2$O is produced about 4% of the time in the chain steps which are:

$$CH_2ClCCl_2O \quad \rightarrow \quad CH_2ClCCl(O) + Cl$$

$$CCl_3CH_2O \quad \rightarrow \quad CH_2O + CCl_3 \overset{O_2}{\rightarrow} CCl_2O + Cl$$

The quantum yield of CO production also increases when O$_2$ is added, but CO is formed only in the initiating and terminating steps.

## Introduction

In earlier reports [1, 2] we examined the reaction of O($^3$P) with C$_2$Cl$_4$ and C$_2$HCl$_3$. In the C$_2$Cl$_4$ system, about 19% of the reaction gave CCl$_2$O, and the remainder gave polymer of C$_2$Cl$_4$O [1]. With C$_2$HCl$_3$, the products were CO, CHCl$_3$, and polymer, the quantum yields of the gas phase products being 0.23 and 0.14, respectively. Both systems gave CCl$_2$ diradicals, and in the presence of O$_2$, the free-radical chain oxidation of C$_2$Cl$_4$ occurred, the initiating reaction being:
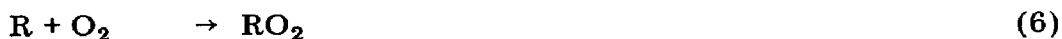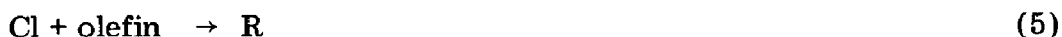
$$CCl_2 + O_2 \quad \rightarrow \quad ClCO + ClO \tag{1}$$

$$ClCO \quad \rightarrow \quad Cl + CO \tag{2}$$

and the possible terminating reactions being:

$$Cl + ClCO \quad \rightarrow \quad Cl_2 + CO \tag{3}$$

$$ClO + ClCO \rightarrow Cl_2O + CO \tag{4a}$$

$$\rightarrow Cl_2 + CO_2 \tag{4b}$$

*Fulbright Fellow.

With $O_2$ present, a long-chain free-radical process occurred, which could be explained with the additional reactions:

$$Cl + olefin \rightarrow R \tag{5}$$

$$R + O_2 \rightarrow RO_2 \tag{6}$$

$$2RO_2 \rightarrow 2RO + O_2 \tag{7a}$$

$$\rightarrow (RO)_2 + O_2 \tag{7b}$$

$$RO \rightarrow 2P_1 + Cl \tag{8a}$$

$$\rightarrow P_2 + Cl \tag{8b}$$

where R represents either radical adduct of Cl and the olefin, $P_1$ represents products containing one carbon atom, and $P_2$ represents products containing two carbon atoms. With $C_2Cl_4$, $P_1$ and $P_2$ were $CCl_2O$ and $CCl_3CCl(O)$, respectively. With $C_2HCl_3$, $P_1$ included both CO and $CCl_2O$, but $P_2$ was exclusively $CHCl_2CCl(O)$.

Reaction (7b) was not important in the $C_2Cl_4$ system, and termination was principally by reactions (3) and (4). However, Cl atoms and presumably ClO react much more rapidly with $C_2HCl_3$ than with $C_2Cl_4$, so that reaction (7b) was an important terminating step in the $C_2HCl_3$ system.

The free-radical oxidation of $CCl_2CH_2$, initiated either by chlorine-atom addition or Hg $6(^3P_1)$ sensitization has been studied by us [3]. In both cases a long chain process was involved in which the major product was $CH_2ClCCl(O)$, and the minor product was $CCl_2O$. The chain steps are reactions (5) - (8b) listed above with reaction (8a) occurring when RO is $CCl_3CH_2O$ and reaction (8b) occurring when RO is $CH_2ClCCl_2O$.

In this report our program on the oxidation of chloroethylenes is extended to the reaction of $O(^3P)$ with $CCl_2CH_2$, both in the presence and absence of $O_2$. The results indicate the same free-radical chain mechanism as for the oxidation of $CCl_2CH_2$ initiated by other routes. The rate law dependence is analogous to the reaction of $O(^3P)$ with the other two chloro-olefins.

Experimental

Oxygen atoms, $O(^3P)$, were prepared from the Hg-photosensitized decomposition of $N_2O$. The experiments were similar to those for $C_2Cl_4$ and $C_2HCl_3$, previously described [1, 2]. The $CCl_2CH_2$ was from J. T. Baker, and the fraction volatile at $-80\,°C$ but condensable at $-130\,°C$ was used. It was degassed before each run at $-130\,°C$. Because it polymerized spontaneously in the storage vessel, it was repurified periodically. The $CH_2ClCCl(O)$ was from Eastman Kodak, the fraction volatile at $-21\,°C$, but condensable at $-80\,°C$, was used. Purification of the other gases has been described previously [1]. The analytical techniques employed were continuous monitoring by infra-red (i.r.) spectroscopy and gas chromatography after irradiation was terminated.

The i.r. technique was the same as used previously [2, 4] for continuous irradiation experiments utilizing three T-shaped cells of lengths 6.6, 9.6, and 12.0 cm across the top of the T. By this method $CCl_2CH_2$ and $CH_2ClCCl(O)$ could be monitored continually from their respective absorption bands at 1640 and 1850 $cm^{-1}$. Peak extinction coefficients (to base 10) for these bands were $4.12 \times 10^{-3}$ and $9.82 \times 10^{-3}$ $Torr^{-1}$ $cm^{-1}$, respectively. $CCl_2O$ was analyzed after the radiation was discontinued, because its i.r. bands were masked by the other species present. The $CCl_2O$ was isolated for analysis in the fraction volatile at $-90\,°C$ but condensable at $-196\,°C$. In runs with $C_2F_4$ present, $CF_2O$ was also monitored by continual i.r. analysis, its peak extinction coefficient at 1960 $cm^{-1}$ being 0.016 $Torr^{-1}$ $cm^{-1}$ (to base 10). The CO and $N_2$ analysis were by gas chromatography after the irradiation was terminated, as previously described [2].

In order to remove the polymer build-up on the i.r. T cell for runs with $O_2$ absent, the cell was rinsed with acetone and isopropanol and dried under vacuum. Since inhibition occurred during the reaction in the presence of $O_2$, the radiation was periodically interrupted and the reaction vessel was shaken. For each run a new Hg drop was used.

## Results

The Hg-photosensitized decomposition of $N_2O$ in the presence of $CCl_2CH_2$ yields $N_2$, CO, $CH_2ClCCl(O)$, polymer, and another unidentified compound as products. There was no evidence for the presence of $CHCl_3$, $CH_2Cl_2$, $CCl_2O$, $C_2Cl_4$, $CCl_2CHCCl_2H$, or $H_2$. In addition, the Hg drop remained clean and bright indicating no $Hg_2Cl_2$ formation.

There was no evidence for $CH_2O$ or HCl, but both of these compounds may be (and probably are) produced. In both cases, their i.r. sensitivity is too low for them to have been detected unless they had large quantum yields. In addition $CH_2O$ polymerizes and cannot be collected or analyzed after the run. HCl is also difficult to separate from $N_2O$ by vacuum distillation, so that other methods of analysis are not easy.

There was also no evidence for $CHCl_2CH(O)$, but if formed with a quantum yield $\leqslant 0.05$, its i.r. bands could have been obscured by those of the unidentified product. In any case $CHCl_2CH(O)$ can only be a minor product, if produced at all. The unidentified product had i.r. bands at 775, 960, 1020, and 1750 $cm^{-1}$, suggesting that it might contain a carbonyl group. It is condensable at $-80\,°C$ and volatile at $-30\,°C$. Possibly this compound could be the epoxide, $\overline{CCl_2CH_2O}$. In any event, its i.r. bands were not prominent, and its quantum yield is probably $< 0.05$.

The quantum yields of $CCl_2CH_2$ disappearance, $-\Phi\{CCl_2CH_2\}$, as well as of CO and $CH_2ClCCl(O)$ production, $\Phi\{CO\}$ and $\Phi\{CH_2ClCCl(O)\}$, respectively, are listed in Table 1. The quantum yields of the products are based on the $N_2$ produced, i.e. on the $O(^3P)$ atom production, rather than the absorbed intensity, $I_a$, measured in separate actinometry experiments, because as polymer accumulates during a run, the light intensity in the

TABLE 1

Reaction of O($^3$P) with CCl$_2$CH$_2$ at 25 °C

| [CCl$_2$CH$_2$]$_0$ [a] (Torr) | [N$_2$O] (Torr) | $I_a$ [b] (mTorr/s) | Irradiation time (s) | $R${N$_2$} [c] (mTorr/s) | $-\Phi${CCl$_2$CH$_2$} [d] | $\Phi${CO} [e] | $\Phi${CH$_2$ClCCl(O)} [e] |
|---|---|---|---|---|---|---|---|
| 1.16 | 243 | 0.50 | 500 | — | 1.3 | 0.36 | — |
| 1.76 | 245 | 0.45 | 1000 | — | 1.6 | 0.38 | — |
| 1.98 | 308 | 0.20 | 2000 | 0.1 | 2.4(2.9) | 0.35 | — |
| 2.07 | 281 | 0.27 | 1720 | — | 2.4 | 0.39 | — |
| 7.46 | 44 | 0.27 | 6158 | — | 2.0 | 0.39 | — |
| 7.47 | 291 | 0.45 | 3100 | — | 2.2 | 0.34 | — |
| 7.57 | 40 | 0.40 | 6383 | — | 1.8 | 0.36 | — |
| 7.85 | 301 | 0.08 | 7000 | 0.04 | 2.5(3.0) | 0.33 | 0.09 |
| 8.30 | 37 | 0.50 | 3476 | — | 1.5 | 0.39 | — |
| 8.41 | 32 | 0.80 | 2000 | 0.21 | 1.1(3.0) | 0.33 | 0.05 |
| 8.41 | 379 | 1.20 | 2000 | 0.47 | 1.1(1.9) | 0.32 | 0.06 |
| 8.60 | 24 | 0.64 | 2200 | 0.14 | 1.4(3.0) | 0.34 | 0.045 |
| 8.62 | 469 | 0.58 | 2200 | 0.27 | 2.3(1.5) | 0.32 | 0.064 |
| 8.84 | 141 | 0.55 | 3039 | — | 2.1 | 0.31 | — |
| 11.50 | 234 | 0.64 | 2500 | — | 2.5 | 0.37 | — |
| 17.75 | 295 | 0.60 | 4050 | — | 1.6 | 0.39 | — |
| | | | | | | Av. = 0.35 | 0.06 |
| | | | | | | ± 0.02 | ± 0.01 |

[a] Initial pressure of CCl$_2$CH$_2$.
[b] $I_a$ at the beginning of the run as determined from the N$_2$ produced in the irradiation of N$_2$O in the presence of 1 - 2% C$_2$F$_4$.
[c] Average rate of N$_2$ production.
[d] $-\Phi${CCl$_2$CH$_2$} based on initial rates. Values in parentheses are ratios of CCl$_2$CH$_2$ consumed to N$_2$ produced at completion of the run.
[e] Quantum yields computed as the ratio of amount of product to amount of N$_2$ produced at completion of run.

reaction cell is reduced. In fact, the data in Table 1 show that the rate of $N_2$ production, $R\{N_2\}$, is always less than $I_a$. The values for $-\Phi\{CCl_2CH_2\}$ are obtained both from initial rates using $I_a$ from separate actinometer experiments and from the final $CCl_2CH_2$ pressure utilizing $N_2$ as an actinometer. The experiments listed in Table 1 encompass values of $[N_2O]$ from 32 to 469 Torr, $[C_2HCl_3]_0$ from 1.16 to 17.75 Torr, and $I_a$ from 0.08 to 1.2 mTorr/s. The quantum yields of $CCl_2CH_2$ disappearance are badly scattered, but are always $> 1$, indicating that more than one $CCl_2CH_2$ molecule is consumed per $O(^3P)$ atom. The results from the two methods of determination are similar, and there is no apparent trend in the data. There is also no apparent trend in either $\Phi\{CO\}$ or $\Phi\{CH_2ClCCl(O)\}$ with any of the experimental parameters, though there is considerable scatter in the data for $\Phi\{CH_2ClCCl(O)\}$. The average values are $\Phi\{CO\} = 0.35 \pm 0.02$ and $\Phi\{CH_2ClCCl(O)\} = 0.06 \pm 0.01$.

In order to measure the rate constant for the reaction of $O(^3P)$ with $CCl_2CH_2$, the Hg-photosensitized decomposition of $N_2O$ was studied in the presence of mixtures of $CCl_2CH_2$ and $C_2F_4$, and both $\Phi\{CO\}$ and $\Phi\{CF_2O\}$ measured. These values are listed in Table 2 for the various experiments. $\Phi\{CF_2O\}$ drops and $\Phi\{CO\}$ rises as the $[CCl_2CH_2]/[C_2F_4]$ ratio is increased, as expected from the competition:

$$O(^3P) + CCl_2CH_2 \rightarrow \alpha CO + \tag{9}$$

$$O(^3P) + C_2F_4 \rightarrow CF_2O + \tag{10}$$

From the results of Table 1, the fraction $\alpha = 0.35$ independent of reaction conditions. Then reactions (9) and (10) lead to the simple rate laws:

$$\Phi\{CO\}/(\Phi_0\{CO\} - \Phi\{CO\}) = k_9[CCl_2CH_2]/k_{10}[C_2F_4] \tag{I}$$

and

$$(\Phi_0\{CF_2O\} - \Phi\{CF_2O\})/\Phi\{CF_2O\} = k_9[CCl_2CH_2]/k_{10}[C_2F_4] \tag{II}$$

where $\Phi_0\{CO\}$ is $\Phi\{CO\}$ in the absence of $C_2F_4$, i.e. $\Phi_0\{CO\} = 0.35$; and $\Phi_0\{CF_2O\}$ is $\Phi\{CF_2O\}$ in the absence of $CCl_2CH_2$, i.e. $\Phi_0\{CF_2O\} = 1.0$ [5]. Figure 1 is a log–log plot of the left-hand sides of eqns. (I) and (II) vs. $[CCl_2CH_2]/[C_2F_4]$. The plot is linear with a slope of one. Its intercept gives $k_9/k_{10} = 1.0$.

In the presence of $O_2$, the major product is $CH_2ClCCl(O)$, and its quantum yield is very much greater than one. Also produced are CO, $CCl_2O$, and HCl, as well as very minor amounts of $CHCl_3$ and polymer. There was no evidence for $CCl_3CH(O)$, $CHCl_2CH(O)$ [$< 1\%$ of $CH_2ClCCl(O)$], $CO_2(\Phi\{CO_2\} < 0.01)$, or the unidentified product formed in the absence of $O_2$, though small amounts of these compounds could have been produced. As before it was not possible to definitely ascertain the presence or absence of $CH_2O$. However, it was not a major product. Polymer production was very small and could only be detected for the run that was carried to completion. Thus in all the runs $R\{N_2\} \simeq I_a$. The Hg drop became coated, but there was no evidence for $Hg_2Cl_2$, as tested by dissolving the drop in nitric acid and adding $AgNO_3$. The coating is presumably HgO formed from

TABLE 2

Reaction of $O(^3P)$ with $CCl_2CH_2$ in the presence of $C_2F_4$ at 25 °C

| $\dfrac{[CCl_2CH_2]}{[C_2F_4]}$ | $[CCl_2CH_2]$ (Torr) | $[C_2F_4]$ (Torr) | $[N_2O]$ (Torr) | Irradiation time (s) | $R[N_2]$ (mTorr/s) | $\Phi[CO]$ [a] | $\Phi[CF_2O]$ [a] |
|---|---|---|---|---|---|---|---|
| 0.30 | 1.95 | 6.50 | 294 | 1550 | 0.88 | 0.063 | 0.83 |
| 0.42 | 1.95 | 4.70 | 300 | 2600 | 0.40 | 0.070 | 0.70 |
| 0.89 | 3.60 | 4.05 | 134 | 1800 | 0.55 | 0.17 | 0.60 |
| 1.00 | 4.00 | 4.00 | 336 | 2000 | 0.59 | 0.18 | 0.54 |
| 1.24 | 4.90 | 3.95 | 509 | 2000 | 0.75 | 0.18 | 0.42 |
| 2.41 | 6.40 | 2.65 | 135 | 3000 | 0.28 | 0.25 | 0.29 |
| 3.70 | 3.70 | 1.00 | 363 | 2200 | 0.26 | 0.28 | 0.20 |
| 6.00 | 7.25 | 1.20 | 422 | 2800 | 0.20 | — | 0.15 |

[a] Quantum yields computed as the ratio of amount of product to amount of $N_2$ produced at completion of the run.
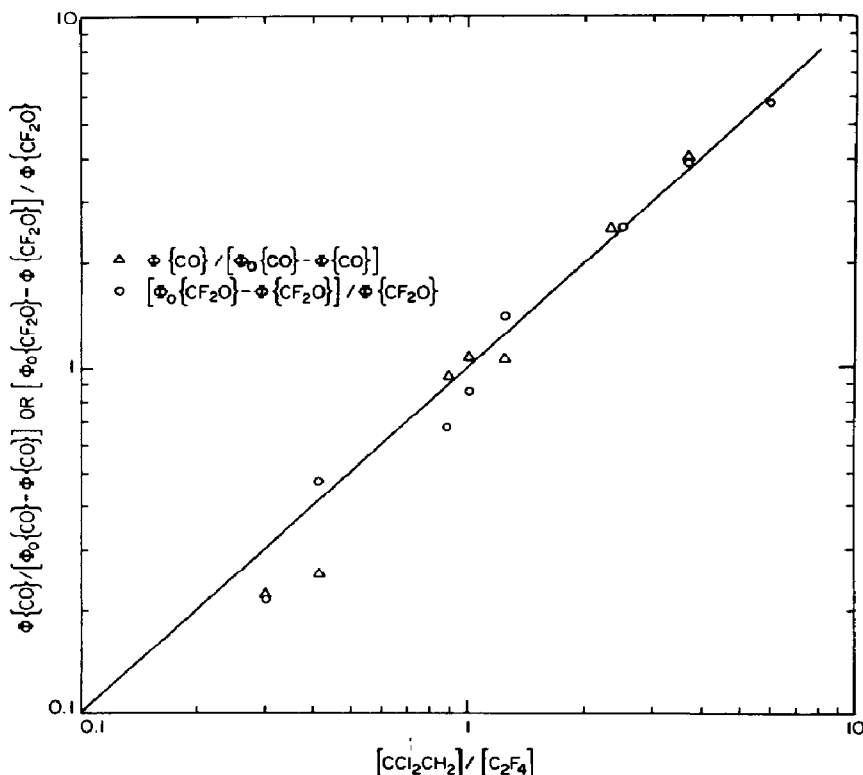
Fig. 1. Log–log plots of $\Phi\{CO\}/(\Phi_0\{CO\} - \Phi\{CO\})$ or $(\Phi_0\{CF_2O\} - \Phi\{CF_2O\})/\Phi\{CF_2O\}$ vs. $[CCl_2CH_2]/[C_2F_4]$ in the Hg-photosensitized decomposition of $N_2O$ in the presence of mixtures of $CCl_2CH_2$ and $C_2F_4$ at 25 °C.

the reaction of Hg and any $O_3$ produced. Therefore, the reaction cell was shaken periodically throughout any experiment to remove the $O_3$.

The results in the presence of $O_2$ are listed in Table 3. The $CCl_2CH_2$ pressure was varied by a factor of 21, the $O_2$ pressure by a factor of 31, $I_a$ by a factor of 9, and the ratio $[CCl_2CH_2]_0/I_a^{1/2}$ by a factor of 21. The results in Table 3 show that the quantum yields increase with $[CCl_2CH_2]/I_a^{1/2}$, except for $\Phi\{CO\}$ which shows no trend with $[CCl_2CH_2]/I_a^{1/2}$. The data for $\Phi\{CO\}$ are badly scattered since CO is such a minor product. However, its average value is 0.78 ± 0.16.

The variation of the quantum yields of the chlorocarbons is shown graphically in Fig. 2. Since $-\Phi\{CCl_2CH_2\}$ and $\Phi\{CH_2ClCCl(O)\}$ are based on initial rates, they are plotted vs. $[CCl_2CH_2]_0/I_a^{1/2}$ in Fig. 2. However, the $CCl_2O$ yields are based on average values, so that the average value of $[CCl_2CH_2]$ was used in Fig. 2. The data are somewhat scattered, but the trend is clear. The log–log plots show less than a linear dependence and seem to indicate upper limiting values for the quantum yields at $[CCl_2CH_2]/I_a^{1/2}$ of $\sim$ 1000 (Torr-s)$^{1/2}$. The relative values of $-\Phi\{CCl_2CH_2\}$, $\Phi\{CH_2ClCCl(O)\}$, and $\Phi\{CCl_2O\}$ are 1.0, 1.0, and 0.032 independent of conditions.

The $CH_2ClCCl(O)$ pressure is shown as a function of irradiation time

TABLE 3
Reaction of O($^3$P) with CCl$_2$CH$_2$ in the presence of O$_2$ at 25 °C

| $\dfrac{[CCl_2CH_2]}{I_a^{1/2}}$ (Torr/s)$^{1/2}$ | [CCl$_2$CH$_2$] [a] (Torr) | [O$_2$] (Torr) | [N$_2$O] (Torr) | $I_a$ [b] (mTorr/s) | Irradiation time (s) | $-\Phi\{CCl_2CH_2\}$ [c] | $\Phi\{CH_2ClCCl(O)\}$ [c] | $\Phi\{CCl_2O\}$ [d] | $\Phi\{CO\}$ [d] |
|---|---|---|---|---|---|---|---|---|---|
| 94 | 1.92(1.41) | 2.7 | 420 | 0.42 | 300 | 17 | 17 | 0.50 | 0.50 |
| 149 | 5.30(3.80) | 5.0 | 360 | 1.25(1.16) | 104 | 28 | 26 | — | — |
| 149[e] | 5.3(4.11) | 5.3 | 355 | 1.25(0.40) | 200 | 27 | 26 | — | — |
| 149[e] | 5.3(4.65) | 14.7 | 365 | 1.25(0.41) | 200 | 28 | 26 | — | — |
| 149[e] | 5.3(4.60) | 45.0 | 335 | 1.25(0.45) | 200 | 19 | 20 | — | — |
| 170 | 3.72(2.80) | 4.9 | 516 | 0.48 | 300 | 18 | 20 | 0.74 | 0.63 |
| 276 | 6.95(5.05) | 3.4 | 529 | 0.69 | 150 | 42 | 40 | 1.2 | 0.98 |
| 280 | 7.34(5.28) | 5.0 | 538 | 0.69 | 150 | 44 | 37 | — | 1.10 |
| 288 | 7.50(5.40) | 37 | 484 | 0.68 | — | 20 | 22 | — | — |
| 309 | 7.75(5.67) | 18 | 554 | 0.63 | 300 | 32 | 30 | — | 0.96 |
| 333 | 6.66(5.29) | 7.2 | 410 | 0.40 | 300 | 30 | 29 | 0.9 | 0.70 |
| 392 | 7.11(6.23) | 1.2 | 461 | 0.33 | 300 | 35 | 40 | 0.8 | 0.81 |
| 433 | 9.50(7.21) | 9.7 | 563 | 0.48 | 307 | 37 | 37 | — | 0.70 |
| 434 | 7.50(5.48) | 10.0 | 365 | 0.30 | 400 | 42 | 40 | 1.0 | 0.80 |
| 436[e] | 7.55(6.70) | 9.9 | 492 | 0.30(~0.1) | 350 | 37 | 37 | <0.6 | 0.55 |
| 476 | 8.25(7.62) | 1.6 | 384 | 0.30 | 130 | 43 | 42 | — | 0.60 |
| 548 | 7.55(6.17) | 9.8 | 562 | 0.19 | 500 | 48 | 40 | 1.5 | 1.00 |
| 622 | 13.9(10.2) | 15 | 540 | 0.50 | 300 | 40 | 39 | — | 0.87 |
| 815 | 17.9(15.8) | 24 | 546 | 0.48 | 300 | 38 | 32 | 1.3 | 0.50 |
| 867 | 7.55(6.6) | 8.3 | 415 | 0.076 | 900 | 58 | 44 | — | 0.73 |
| 2000 | 40(—) | 23 | 334 | 0.40 | — | 55 | 50 | —[f] | —[f] |

Av. = 0.78 ± 0.16

[a] Initial CCl$_2$CH$_2$ pressures. The values in parentheses are average values for the irradiation.
[b] $I_a$ is the average value determined by N$_2$ formation during the run and in separate actinometer experiments. The difference between the two values are always less than the experimental uncertainty, when the cell was shaken periodically. When the cell was not shaken, the first value is initial $I_a$ and the value in parenthesis is the average $I_a$ (from N$_2$ measurement).
[c] Based on initial rates.
[d] Based on the ratio of the amount of product to amount of N$_2$ at completion of the run.
[e] Reaction cell not shaken during the irradiation.
[f] 100% conversion of CCl$_2$CH$_2$: [CCl$_2$CH$_2$]$_0$/[CCl$_2$O] ~ 40, [CCl$_2$CH$_2$]$_0$/[CCl$_3$H] ~ 260. Solid coated the reaction vessel.

8
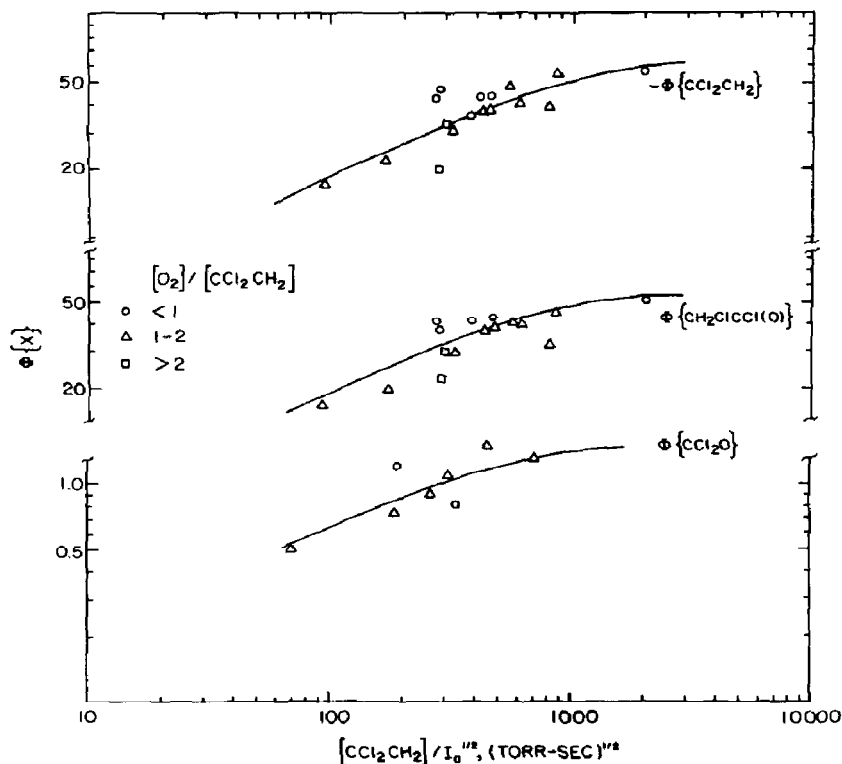
Fig. 2. Log–log plots of the quantum yields *vs.* $[CCl_2CH_2]/I_a^{1/2}$ in the reaction of $O(^3P)$ with $CCl_2CH_2$ in the presence of $O_2$ at 25 °C. For $CCl_2CH_2$ and $CH_2ClCCl(O)$, initial values of $[CCl_2CH_2]$ were used in the computations; for $CCl_2O$, average values of $[CCl_2CH_2]$ were used.

for four comparable runs in Fig. 3. In three runs with different $O_2$ pressures the reaction cell was not shaken, whereas in the other the irradiation was interrupted periodically and the reaction vessel shaken. When the cell was not shaken, less $CH_2ClCCl(O)$ is produced, indicating inhibition. The inhibition is more marked as the $O_2$ pressure is increased. In addition $N_2$ production is also inhibited.

Discussion

The $O(^3P)$ atoms are produced by Hg photosensitization:

$$Hg + h\nu \quad \rightarrow \quad Hg^{\star} \tag{11}$$

$$Hg^{\star} + N_2O \quad \rightarrow \quad Hg + N_2 + O(^3P) \tag{12}$$

The possible reaction paths between $O(^3P)$ and $CCl_2CH_2$ are:

$$O(^3P) + CCl_2CH_2 \rightarrow \quad CCl_2O + CH_2 \tag{9a}$$

$$\rightarrow \quad CH_2O + CCl_2 \tag{9b}$$

$$\rightarrow \quad CO + HCl + CHCl \tag{9c}$$

$$\rightarrow \quad CO + Cl_2 + CH_2 \tag{9d}$$
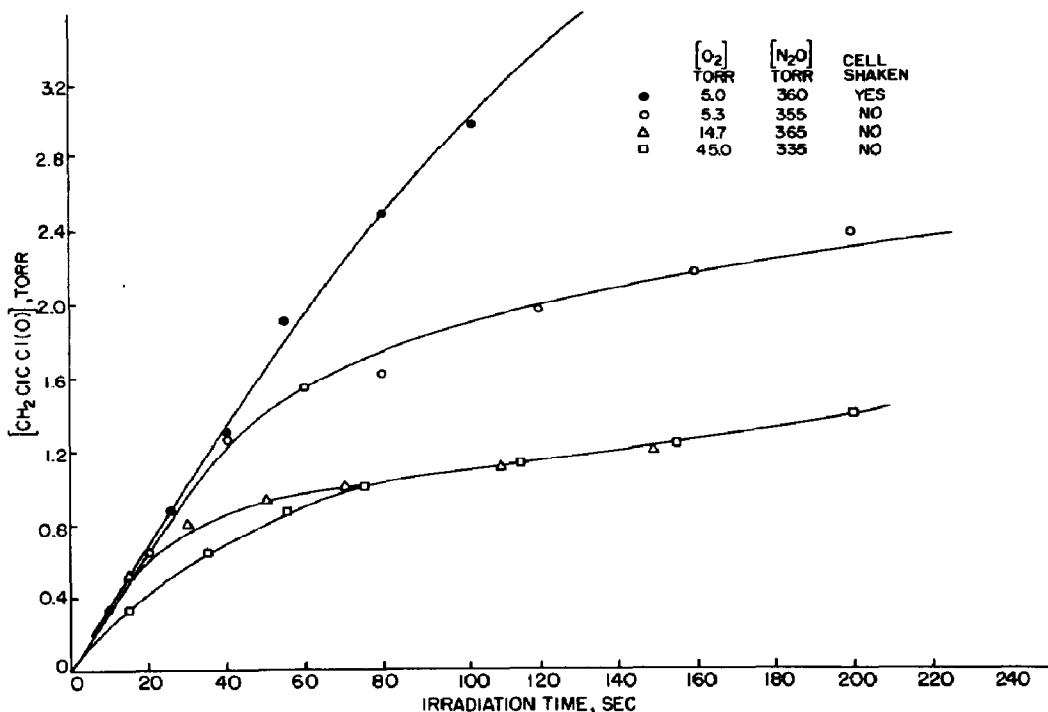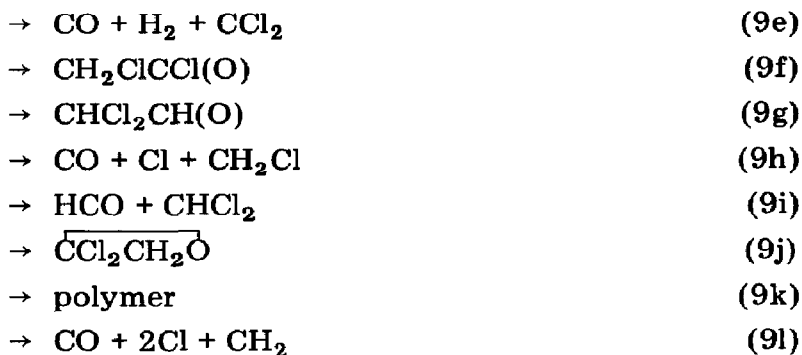
Fig. 3. Plot of the $CH_2ClCCl(O)$ pressure *vs.* irradiation time for four comparable runs in the reaction of $O(^3P)$ with $CCl_2CH_2$ with $[CCl_2CH_2]_0$ = 5.3 Torr in the presence of $O_2$ at 25 °C, and an initial $I_a$ = 1.25 mTorr/s. In three runs the irradiation was continuous and the reaction cell was not shaken. In the other run, the radiation was interrupted after each reading to shake the reaction cell.

$$\rightarrow \; CO + H_2 + CCl_2 \qquad\qquad (9e)$$

$$\rightarrow \; CH_2ClCCl(O) \qquad\qquad (9f)$$

$$\rightarrow \; CHCl_2CH(O) \qquad\qquad (9g)$$

$$\rightarrow \; CO + Cl + CH_2Cl \qquad\qquad (9h)$$

$$\rightarrow \; HCO + CHCl_2 \qquad\qquad (9i)$$

$$\rightarrow \; \overline{CCl_2CH_2O} \qquad\qquad (9j)$$

$$\rightarrow \; polymer \qquad\qquad (9k)$$

$$\rightarrow \; CO + 2Cl + CH_2 \qquad\qquad (9l)$$

Some of the above reactions would probably proceed through energetic intermediates. Certainly this would be true for those yielding three fragments. Some of these reactions can be ruled out immediately because a product was not found. In particular, $CCl_2O$, $Cl_2$, $H_2$, $CHCl_2CH(O)$ and probably $\overline{CCl_2CH_2O}$ (unless it is the unidentified product) were not produced. Consequently reactions (9a), (9d), (9e), (9g), and (9j) are unimportant. Of the remaining, only three, reactions (9c), (9h), and (9l) produce CO, so together they must account for 35% of the reaction. Channel (9f) accounts

for 6% of the reaction since it is the only route to $CH_2ClCCl(O)$ production in the absence of $O_2$. The remaining fraction of the reaction can be attributed to reaction paths (9b), (9i), and (9k). Reaction (9f) is an abnormal reaction in that chlorine atom transfer is required. Apparently such a process occurs in the $O_3 - C_2Cl_4$ [6] and $O_3 - CCl_2CH_2$ [7] reactions, but we know of no other examples of such a process at room temperature. That this reaction occurs is even more unusual since the H-atom transfer reaction to produce $CHCl_2CH(O)$ does not occur.

More information on the probability of each of the reaction paths can be obtained by considering $\Phi\{CO\}$ in the absence and presence of $O_2$, which is 0.35 and 0.78, respectively. Since the invariance of $\Phi\{CO\}$ to $[CCl_2CH_2]/I_a^{1/2}$ in the presence of $O_2$ indicates that CO is not formed in the chain process, then all the additional CO in the presence of $O_2$ comes from oxidation of the radical fragments from reaction (9). The oxidation of HCO and $CH_2$ leads to CO production directly:

$$HCO + O_2 \quad \rightarrow \quad HO_2 + CO \tag{13}$$

$$CH_2 + O_2 \quad \rightarrow \quad CO + H_2O \tag{14}$$

The oxidation of $CCl_2$ [1, 2] and CHCl [8] leads to CO through ClCO formation:

$$CCl_2 + O_2 \quad \rightarrow \quad ClO + ClCO \tag{1}$$

$$CHCl + O_2 \quad \rightarrow \quad HO + ClCO \tag{15}$$

The ClCO then gives CO *via* reactions (2), (3) or (4a). With $CHCl_2$ and $CH_2Cl$ [9], the oxidation product is CHClO which decomposes to CO [10].

All the reaction channels and the CO production from these channels in the absence and presence of $O_2$ are listed in Table 4. Since the sum of the efficiencies of reactions (9c), (9h), and (9l) must equal 0.35, and they each produce two CO molecules in the presence of $O_2$, the remainder of the CO in the presence of $O_2$ (*i.e.* 0.08) must come from reactions (9b) and (9i).

At high $[CCl_2CH_2]/I_a^{1/2}$ in the presence of $O_2$, $-\Phi\{CCl_2CH_2\}$ approaches 60, *i.e.* 35% of the value of 172 found in the chlorine-atom or Hg 6 ($^3P_1$) photosensitized studies. In each of those studies two chain carriers were produced for each photon absorbed. Consequently in this study the efficiency of chain carrier production must be 0.70. In Table 4, the number of chain carriers for the oxidation are listed for each process. Of the five possible processes that can produce CO and chain carriers [*i.e.* reactions (9b), (9c), (9h), (9i) and (9l)] they must occur in combinations such that: (1) $\Phi\{CO\}$ = 0.35 in the absence of $O_2$; (2) $\Phi\{CO\}$ = 0.78 in the presence of $O_2$; (3) the efficiency of chain carrier production is 0.70. The limiting values for the quantum efficiencies of the five processes that meet these requirements are given in Table 4.

There is another piece of information pertaining to the relative importance of the paths in reaction (10). $CHCl_3$ was found as a product in the $C_2HCl_3$ system [2]. Presumably it comes from reaction between $CCl_2$ and HCl. In the $CCl_2CH_2$ system, $CHCl_3$ was not a product in the absence of
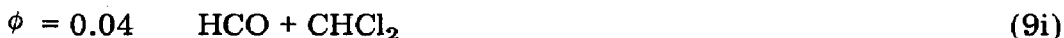
TABLE 4

Possible products from the reaction of $O(^3P)$ with $CCl_2CH_2$

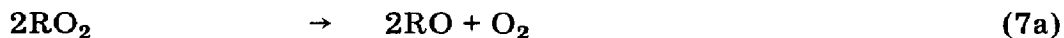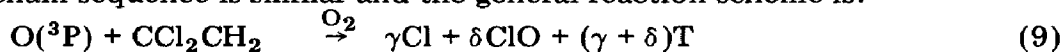| Reaction | Products | Probability | No. of CO produced | | Chain carriers [b] |
|----------|----------|-------------|-----------|------------|-----------------|
| | | | $O_2$ absent | $O_2$ present | |
| 9a | $CCl_2O + CH_2$ | $0$ [a] | 0 | 1 | 0 |
| 9b | $CH_2O + CCl_2$ | $\leqslant 0.08$ | 0 | 1 | 2 |
| 9c | $CO + HCl + CHCl$ | $\leqslant 0.31$ | 1 | 2 | 2 |
| 9d | $CO + Cl_2 + CH_2$ | $0$ [a] | 1 | 2 | 0 |
| 9e | $CO + H_2 + CCl_2$ | $0$ [a] | 1 | 2 | 2 |
| 9f | $CH_2ClCCl(O)$ | 0.06 | 0 | 0 | 0 |
| 9g | $CHCl_2CH(O)$ | $0$ [a] | 0 | 0 | 0 |
| 9h | $CO + Cl + CH_2Cl$ | 0.04 - 0.16 | 1 | 2 | 1 |
| 9i | $\overline{HCO + CHCl_2}$ | $\leqslant 0.04$ | 0 | 2 | 1 |
| 9j | $\overline{CCl_2CH_2O}$ | $0$ [a] | 0 | 0 | 0 |
| 9k | Polymer | 0.51 - 0.55 | 0 | 0 | 0 |
| 9l | $CO + 2Cl + CH_2$ | $\leqslant 0.31$ | 1 | 2 | 2 |

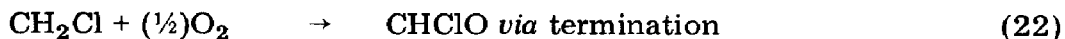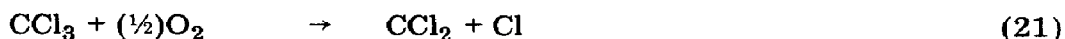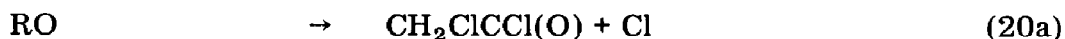[a] Detection limit is about 5%.
[b] With $O_2$ present.

$O_2$ thus inferring that both HCl and $CCl_2$ are not present, *i.e.* that reactions (10b) and (10c) are not both operative.

Finally, there is one further piece of information to consider. The rate law in the presence of $O_2$ requires that for every Cl or ClO produced, a "terminating" radical must also be produced. Thus reaction (9l) cannot be important. We consider the likely primary fragments and their yields to be:

$$\phi = 0.31 \quad CO + HCl + CHCl \tag{9c}$$

$$\phi = 0.04 \quad CO + Cl + CH_2Cl \tag{9h}$$

$$\phi = 0.04 \quad HCO + CHCl_2 \tag{9i}$$

With $O_2$ present, the chain products are $CH_2ClCCl(O)$ and $CCl_2O$. The overall rate law is different from those in the chlorine atom and Hg $6(^3P_1)$ sensitized oxidations [3]. However, the rate law is similar to those in the $C_2Cl_4$ and $C_2HCl_3$ reactions with $O(^3P)$ in the presence of $O_2$. Presumably the chain sequence is similar and the general reaction scheme is:

$$O(^3P) + CCl_2CH_2 \xrightarrow{O_2} \gamma Cl + \delta ClO + (\gamma + \delta)T \tag{9}$$

$$T + Cl \rightarrow \text{termination} \tag{16}$$

$$T + ClO \rightarrow \text{termination} \tag{17}$$

$$Cl + CCl_2CH_2 \rightarrow R \tag{18}$$

$$R + O_2 \rightarrow RO_2 \tag{6}$$

$$2RO_2 \rightarrow 2RO + O_2 \tag{7a}$$

$$\rightarrow \text{termination} \tag{7b}$$

$$\text{ClO} + \text{CCl}_2\text{CH}_2 \quad \rightarrow \quad \text{RO} \tag{19}$$

$$\text{RO} \quad \rightarrow \quad \text{CH}_2\text{ClCCl(O)} + \text{Cl} \tag{20a}$$

$$\rightarrow \quad \text{CCl}_3 + \text{CH}_2\text{O} \tag{20b}$$

$$\text{CCl}_3 + (\tfrac{1}{2})\text{O}_2 \quad \rightarrow \quad \text{CCl}_2 + \text{Cl} \tag{21}$$

$$\text{CH}_2\text{Cl} + (\tfrac{1}{2})\text{O}_2 \quad \rightarrow \quad \text{CHClO } via \text{ termination} \tag{22}$$

where reaction (9) is now an overall reaction; T represents the terminating radicals $\text{HO}_2$, $\text{ClCO}$, $\text{CH}_2\text{Cl}$ and $\text{HCO}$; R is either radical adduct of Cl and $\text{CCl}_2\text{CH}_2$; and for simplicity reaction (22) is an overall reaction representing the fate of $\text{CH}_2\text{Cl}$ [9]. Also, reaction (9) may produce HO radicals *via* oxidation of CHCl [8] and these would then add to $\text{CCl}_2\text{CH}_2$. This would lead to a similar chain, resulting in no mechanistic alteration. For reaction (20), it should be realized that (20a) is the decomposition path if RO is $\text{CH}_2\text{ClCCl}_2\text{O}$, and that reaction (20b) is the decomposition path if RO is $\text{CCl}_3\text{CH}_2\text{O}$.

The mechanism leads to the predictions that if the termination is primarily by reaction (7b) and not by reactions (16) and (17), *i.e.* at high $[\text{CCl}_2\text{CH}_2]/I_a^{1/2}$, and if the chains are long, then:

$$-\Phi\{\text{CCl}_2\text{CH}_2\} = 1 + k_7 k_{20}/k_{7b}k_{20a} \simeq k_7 k_{20}/k_{7b}k_{20a} \tag{III}$$

$$\Phi\{\text{CH}_2\text{ClCCl(O)}\} = 0.06 + k_7/k_{7b} \simeq k_7/k_{7b} \tag{IV}$$

$$\Phi\{\text{CCl}_2\text{O}\} = (k_7/k_{7b})(k_{20b}/k_{20a}) \tag{V}$$

In accordance with the prediction, the quantum yields become independent of $[\text{CCl}_2\text{CH}_2]/I_a^{1/2}$ at high values of $[\text{CCl}_2\text{CH}_2]/I_a^{1/2}$. The observed ratio for $\Phi\{\text{CCl}_2\text{O}\}/\Phi\{\text{CH}_2\text{ClCCl(O)}\} = 0.032$ gives $k_{20b}/k_{20a} = 0.032$.

If the termination is mainly by reactions (16) and (17), rather than by reaction (7b), *i.e.* if $[\text{CCl}_2\text{CH}_2]/I_a^{1/2}$ is small, and if the chains are long, then the mechanism gives:

$$-\Phi\{\text{CCl}_2\text{CH}_2\} = 1 + \epsilon k_{18} \frac{k_{20}[\text{CCl}_2\text{CH}_2]}{k_{20a}I_a^{1/2}} \approx \epsilon k_{18} \frac{k_{20}[\text{CCl}_2\text{CH}_2]}{k_{20a}I_a^{1/2}} \tag{VI}$$

$$\Phi\{\text{CH}_2\text{ClCCl(O)}\} = 0.06 + \epsilon k_{18} \frac{[\text{CCl}_2\text{CH}_2]}{I_a^{1/2}} \approx \epsilon k_{18} \frac{[\text{CCl}_2\text{CH}_2]}{I_a^{1/2}} \tag{VII}$$

$$\Phi\{\text{CCl}_2\text{O}\} = \epsilon k_{18} \frac{k_{20b}[\text{CCl}_2\text{CH}_2]}{k_{20a}I_a^{1/2}} \tag{VIII}$$

where

$$\epsilon^2 \equiv \frac{(\gamma + \delta)}{\left(1 + \dfrac{k_{20b}}{k_{20}}\dfrac{k_{18}}{k_{19}}\right)\left(k_{16} + \dfrac{k_{17}k_{18}}{k_{19}}\dfrac{k_{20b}}{k_{20a}}\right)}$$

The quantum yields become proportional to $[\text{CCl}_2\text{CH}_2]/I_a^{1/2}$. From Fig. 2, it

can be seen that this regime is never fully operative, but the drop-off from the upper limiting value is apparent at the lowest values of $[CCl_2CH_2]/I_a^{1/2}$. This behavior is almost identical to that found in the $C_2HCl_3$ system [2] and suggests that the rate coefficients for Cl-atom and/or ClO addition to the two olefins $C_2HCl_3$ and $CCl_2CH_2$ are similar. Otherwise the cross-over between the two terminating regimes would occur under different conditions. Again the ratio of quantum yields gives $k_{20b}/k_{20} = 0.032$, exactly as before.

Even though the ratio of quantum yields gives $k_{20b}/k_{20} = 0.032$, this value is significantly higher than the value of $\sim 0.01$ found in the chlorine-atom and Hg $6(^3P_1)$ oxidations of $CH_2CCl_2$ [3]. Possibly the error reflects experimental uncertainty, since the $CCl_2O$ is produced as a minor product. Alternatively there may be an additional route to $CCl_2O$ production in the $O(^3P) + CCl_2CH_2 + O_2$ system which we have not considered.

Finally, we comment on the inhibition observed as the reaction proceeds, if the reaction cell is not shaken, as illustrated in Fig. 3. One possibility is that the inhibition could be attributed to $O_3$ formation which could inhibit the free-radical chain oxidation, as it does with $C_2Cl_4$ [1]. The coating of the Hg drop, which could be HgO, supports this hypothesis. However, the importance of $O_3$ production can be estimated from the competition between reaction (9) and:

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (23)$$

The rate coefficient for reaction (23) is about $2 \times 10^8$ $M^{-2}$ $s^{-1}$ at 25 °C [11]. Since $k_9/k_{10} = 1.0$ and $k_{10} = 6 \times 10^8$ $M^{-1}$ $s^{-1}$ [5], then $k_9 = 6 \times 10^8$ $M^{-1}$ $s^{-1}$. For our experiments $[N_2O] \sim 0.023$ $M$, so that reaction (23) is $< 1\%$ as important as reaction (9) for $[O_2]/[CCl_2CH_2] = 1.3$. Consequently $O_3$ production does not appear to be the cause of the inhibition, and we have no explanation for this phenomenon.

## Acknowledgement

## References

1  E. Sanhueza and J. Heicklen, Center for Air Environment Studies Rep. No. 305-73, Penn. State University (1973); Can. J. Chem., 52 (1974) 3870.
2  E. Sanhueza and J. Heicklen, Center for Air Environment Studies Rep. No. 316-73, Penn. State University (1973); Int. J. Chem. Kinet., 6 (1974) 553.
3  E. Sanhueza and J. Heicklen, Center for Air Environment Studies Rep. No. 353-74, Penn. State University (1974); J. Photochem., in press.
4  E. Sanhueza and J. Heicklen, Center for Air Environment Studies Rep. No. 306-73, Penn. State University (1973); Can. J. Chem., 52 (1974) 3863.
5  J. Heicklen, Adv. Photochem., 7 (1969) 57.
6  E. Mathias, E. Sanhueza, I. C. Hisatsune and J. Heicklen, Center for Air Environment Studies Rep. No. 304-73, Penn. State University (1973); Can. J. Chem., 52 (1974) 3852.
7  L. A. Hull, I. C. Hisatsune and J. Heicklen, Can. J. Chem., 51 (1973) 1504.

8  E. Sanhueza and J. Heicklen, Center for Air Environment Studies Rep. No. 364-74, Penn. State University (1974); Int. J. Chem. Kin., in press.
9  E. Sanhueza and J. Heicklen, Center for Air Environment Studies Rep. No. 349-74, Penn. State University (1974); J. Phys. Chem., in press.
10 I. C. Hisatsune and J. Heicklen, Center for Air Environment Studies Rep. No. 309-73, Penn. State University (1973); Can. J. Spectrosc., 18 (1973) 77.
11 S. W. Benson and W. De More, A. Rev. Phys. Chem., 15 (1965) 397.